TRANSACTIONS
OF THE
AMERICAN INSTITUTE
OF
CHEMICAL ENGINEERS

VOLUME XXX

1933-34

Containing papers read at

Roanoke, Virginia
December 12, 13, 14, 1933

and

New York, New York
May 14, 15, 16, 1934

OFFICE OF THE EXECUTIVE SECRETARY
BELLEVUE COURT BUILDING
Philadelphia, Pa.

PUBLISHED BY THE INSTITUTE
AND FOR SALE BY
D. VAN NOSTRAND COMPANY, INC.
NEW YORK
1934

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Printers and Electrotypers
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Printed in U.S.A.

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AMORTIZATION, DEPRECIATION, OBSOLESCENCE AND REPLACEMENT

By WYMAN P. FISKE*

I. Introduction

Declining prices, unsatisfactory volumes, new developments and inventions, and drastic changes in style and in engineering aspects of product have all occupied a central position in the industrial picture during the last four difficult years. Now the National Recovery Act adds the possibility of prorated and limited production, and makes pointed reference to the unsoundness, unfairness and possible illegality of selling below cost. Manufacturers are being urged to modernize methods and plants as a part of the "buy now" campaign. All of these problems affect the manufacturer's equipment policy and are reasons for a careful reconsideration of such policy. Recent trends in price levels plus the national administration's attitude in regard to the desirability of further increases and the recent enactment of an excess profits tax have probably put an end to the wave of write-downs which swept the country during the past year and a half. (Indeed some of those most anxious to write down will probably be in the forefront equally anxious to write up.) Other problems of equal importance remain. What is "cost" so far as equipment is concerned? How will manufacturing cost be affected by possible proration of production and by obsolescence arising from new inventions and change of products and processes? To what extent should new equipment be purchased to replace old? Where is the money coming from? These and other questions are a part of any sound equipment policy and must be solved correctly if the enterprise is to prosper.

A sound equipment policy must be based upon a foundation of accounting and financial concepts and relationships. These concepts and relationships should be a part of the working equipment not only of management, which must make the decisions, but also of all those

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concerned with any aspect of the problem. In particular the engineering profession, which will design equipment and initiate suggestions as to new methods and processes, should have a complete understanding of these fundamentals, in order that designs and suggestions may stand the test of business practicability. It is no less inexcusable for a well-trained engineer to recommend a new machine which will result in higher costs than for the same engineer to design a bridge which is structurally sound but does not have sufficient clearance to permit a train to pass through or over it.

Much textual and periodical material is available on various aspects of equipment policy. A considerable part of this material has been written in technical terms for the professionally trained accountant and is therefore confusing to men without accounting training. It is the object of this paper to restate the basic concepts and relationships involved in the replacement aspects of equipment policy and to state the fundamentals of a sound approach to the economics of choice between alternative equipments or processes. In passing, some of the common mistakes and fallacies will be pointed out. Such little value as the paper may have will arise not from any new or startling principles, but from a clearer statement in simple non-technical terms of ideas that are old but often misunderstood or forgotten.

II. What are Costs?

The object of all business enterprise is profit, and the determination of net income or profit is one of the major tasks of every accounting department. Although the only strictly correct definition of business net income is "an increase in net worth (the excess of assets over debt) resulting from any cause other than new investments by proprietary (owners') interests," the more common definition and method of determination is the balance of income remaining after deducting from gross income all expenses, including items accrued but not paid. An important element in equipment policy is the provision for inclusion in expenses of proper amounts to cover the costs arising from the use of plant and equipment. A brief consideration of the nature and sources of expenses is accordingly relevant and prerequisite to any understanding of depreciation, obsolescence and repairs.

Expenses consist of goods or services utilized in production and in sale of the goods or services sold as well as those utilized in the financ-

ing and administration of the enterprise. Expenses include all values given up in the exchange transaction which we call the sale; they include not only the goods sold but in addition values expended in making the sale. A business is composed of five elements: (a) a place to work, (b) machines and tools to work with, (c) men to do the work, (d) material to work on, and (e) management to coördinate the whole. These elements and the financing involved in procuring them give rise to business costs. Costs are thus outlays for shelter (rent * or taxes, insurance, depreciation and repairs on buildings); for machines (royalties or taxes, insurance, and depreciation on machinery, repairs and power); for labor (wages of productive and service employees); for materials used in the product, supplies and packing; for management (supervision and administrative salaries); and for cost of borrowed capital (interest on bank loans and bonds or notes).

There is no necessary relation between cash expenditures and expenses. While it is true that most expense items are offset or represented by practically coincidental † cash expenditures, some important ones may arise from quite different sources. Goods or services may equally well be purchased with credit or non-cash assets. If credit is accepted by the seller, title to the goods passes to the buyer (unless reserved in the sales agreement) and cannot be recovered even if the buyer defaults on payment; legal redress lies only in a suit to recover the amount due. Occasionally goods are bought and paid for by giving up assets other than cash, as where used equipment is tendered as partial or complete payment for new equipment. Failure to recognize the several sources of expenses has led to much false reasoning based on the misconception that costs must be related to outlays of cash.

Goods or services used up in business operation may be purchased either at approximately the time of use or well in advance of use. Marked advantage often comes from purchase in large quantities in advance of requirements. In the previous paragraph it was pointed out that the method of payment does not affect the nature of an item as a cost. Neither does the time of purchase affect it. Goods or services purchased in advance of requirement are expense when used just as much as goods or services purchased and immediately used. Materials, insurance protection, shelter and machine operations are

* Expense items listed are illustrative but not complete.

† Within ten to thirty days.

commonly bought in advance in the form of inventories, prepaid insurance policies, buildings or leasehold rights and machinery or prepaid royalties. Payroll, purchased power and such items are ordinarily bought as required, payroll and power for the obvious reason that they cannot be stored.

The accountant assembles expenses from three sources. (1) The majority of expense items represent purchases for immediate use, billed as shipped and paid for within periods ranging from ten days to one or two months. (2) Some items, like bond interest, taxes and book royalties are payable only at considerable intervals and are not billed as used. Expenses of this type must be accrued; that is, both the expense and the future obligation must be recorded in order that the cost may be included in the profit and loss statement and the liability in the balance sheet. This group is referred to as accruals. Both this and the previous group are made up of items bought as used; the distinction lies in the custom of billing and payment. (3) The third class includes expenses arising from utilization of goods or services bought in advance of requirement. An example is fire insurance which is bought in advance of protection. The cost of such protection is an expense for the period during which it is received regardless of when or how it is paid for. The utilization or expiration of such prepaid expenses must, like accruals, be recorded if profits and the balance sheet are to be correct. The problem of distinguishing between so-called capital and revenue charges is thus in reality a problem of distinguishing between assets and expense. A basis for the distinction and for understanding the nature of amortization, depletion, depreciation and obsolescence is recognition of the fact that all assets except cash, cash equivalents (call loans, government securities, etc.), receivables and investments are in reality inventories of prepaid services or expenses arising in connection with the apportionment of such services or expenses between accounting periods.

III. Amortization, Depletion, Depreciation and Obsolescence

All assets except cash, cash equivalents, receivables, investments, intangibles of the nature of goodwill, and land used merely as a location for an industrial enterprise, eventually become expense as they are consumed in use. Inventories, prepaid insurance, buildings, machinery and equipment are all prepaid expenses, representing in each case materials or services purchased in advance of use for eventual

consumption in the operations of the business. These assets differ only in the rapidity of utilization in production and distribution. Materials are ordinarily completely used up in a single cycle of business operation.* Buildings, machinery and equipment, on the other hand, provide service for varying lengths of time but always for a period in excess of one operating cycle. This difference in rate of utilization does not change the essential nature both of inventories and of plant as prepaid expenses ultimately to be charged as expenses of the accounting period or periods which benefit from the service rendered. The process of apportioning these various prepaid expenses to the period benefited is variously referred to as amortization, depletion and depreciation according to the type of asset (prepaid expense) involved. The term "amortization" is used in the case of such intangibles as prepaid interest, prepaid insurance, and prepaid rent and leaseholds. "Depletion" applies to wasting natural resources, as mines and oil wells. "Depreciation" is used where physical plant (buildings, machinery and equipment) is involved. All three terms refer to the process of apportioning prepaid expenses of various kinds to the proper accounting periods. It should be noted carefully that if the accounting period were increased in length to the life of buildings and machinery, capital charges on the one hand and amortization, depletion and depreciation on the other would all tend to disappear since machines and buildings completely consumed within the accounting period would become expenses of the period and would be charged as such at the time of purchase. Capital charges, and amortization, depletion and depreciation thus become necessary as means of apportioning the cost of productive capacities to the periods actually benefited.

Most business men accept without question the necessity of prorating the cost of prepaid insurance policies over the periods during which the protection is in force. Likewise there is necessity for amortizing prepaid rent or interest, the cost of leaseholds (merely another form of prepaid rent) or bond discount (part of the cost of borrowed capital). Patents represent prepaid royalties, the cost of which must be charged to the product benefited. Amortization is the term applied to the process of charging to each accounting period

* "Cycle of business operation" refers to the flow of funds into goods and services which in production are converted into salable goods; these goods are then converted into receivables through sale and then into cash through collection of the receivables. The cycle then repeats itself.

proper portions of the original amount of intangible prepayments of the type indicated above.

Depletion is essentially the simplest of the three concepts. It is subject neither to the intangibility of amortization of rights to insurance protection or use of a given process, nor to the indefiniteness (only apparent) of depreciation. Mines and oil wells are bought on the basis of an estimate of the ultimate yield of coal, ore or oil. Obviously the removal of every ton of coal or barrel of crude oil leaves a smaller quantity still to be recovered. Equally obviously a charge must be made to expense for the depletion of the reserves, since when the last ton or barrel is removed, the value of the mine or well will have disappeared;* unless it has been recovered in the price of the product the capital of the enterprise will have been dissipated. The cost of the product must include a depletion element, representing the same proportion of the original cost which the weight or volume of the product removed bears to the original amounts purchased.

The intangibility of such assets as leaseholds and patents has caused much false reasoning. Likewise the very physical definiteness of buildings, machinery and equipment has been an important source of misconceptions. The concept of a building, machine or piece of equipment as capacity for so much shelter, for so many operations or for so much service is of assistance not only in determining an outlay to have been for an asset as opposed to an expense item, but also in understanding the concept of depreciation. Thus an outlay for a truck is in reality an outlay for so many ton-miles of transportation rather than an outlay for a physical object. Every ton-mile produced reduces the service capacity of the truck and every operation performed by a machine reduces the capacity of that machine. The mistakes arising from attaching an undue weight to physical condition of plant items will be discussed in a later paragraph.

The use of buildings, machinery and equipment gives rise to two forms of special expense directly attributable to these items, repairs and depreciation. As to these items there has been, and still is, as much loose thinking and general misunderstanding as exists in regard to any accounting or financial concept. This misunderstanding is particularly regrettable because, coupled with the financial significance of repairs and depreciation as expense items, it has resulted in much bad financial policy. The basic reasons for most of the loose reason-

* This assumes no residual value.

ing are failure to appreciate the fundamental nature of the plant item on the balance sheet as prepaid expense and failure to appreciate that the purchase price is in reality given in exchange for a definite service capacity rather than for a material object answering to certain specifications. As soon as these concepts become clear it is fairly obvious that such a prepaid expense must ultimately be apportioned to the periods or production benefiting, until finally the total cost shall have been charged to operations. Depreciation is cost of expired plant capacity.

Much of the misunderstanding has also been due to defining depreciation as a loss in value. This definition emphasizes dollars rather than productive capacity and unfortunately suggests a relation between depreciation and market value. Depreciation might be defined as a loss in service value or service capacity. The necessity for a common denominator in accounting records forces the accountant to reduce this loss in service value to dollars; the basis of determining dollars of depreciation is ordinarily cost rather than market value of the service capacity used. Market value is a factor only to the extent that at the date of original purchase it coincides with cost and that at the date of retirement it determines scrap or recovery value. The total amount to be amortized or depreciated is the difference between original cost and scrap value at date of retirement. The business man is interested in the cost of the service received, based on what he paid, not on later price fluctuations.

A further cause for general misunderstanding is the tendency of some writers to confuse depreciation with loss in engineering efficiency. That many engineers should be led astray in their reasoning by this confusion may be understandable; it is nevertheless unfortunate. The following statement is typical of the fallacies resulting. "No piece of machinery can depreciate below say thirty per cent of its cost new. There is a point below which it is practically impossible to operate a machine and this is seldom less than seventy per cent. Hence any attempt to place a valuation on a property of less than seventy per cent of cost is absurd." The point from which this reasoning starts, namely that "there is a point below which it is practically impossible to operate a machine," is sound and refers to the engineering fact that operation below a certain point of operating efficiency is not economically practicable. The conclusion is unwarranted because the author has utterly failed to recognize that as soon as decreasing plant efficiency prevents further economical operation of a machine

then the service capacity of that machine has reached zero. All possible use has been obtained and the total original cost of the machine (less recoverable scrap) should have been charged to operations. Even though the machine is still seventy per cent efficient there is no future benefit in the form of productive capacity and thus no justification for showing a value for the item on the balance sheet. There is no asset. The error in the statement reproduced would have been avoided had the author fully appreciated that depreciation is a charge representing the utilization and consumption in business operations of a portion or all the service capacity of plant items just as material cost represents the utilization and consumption in business operations of material. Depreciation is one part of plant expense.

It is really difficult to understand why the fact of depreciation as an expense should ever have been questioned. The very individuals who have argued most strongly against this point recognize the necessity of including as expense and as part of the cost of production material, supplies and small perishable tools. If the sheet metal portions of ten articles can be stamped out of a single sheet the cost of that sheet less recoverable scrap is prorated over the ten articles in question. If the die used in the stamping operation will be worn out in seventy-five hundred operations the cost of the finished article will include an element representing one seventy-five hundredth of the cost of the die. By the same logic if the press itself will have become useless after a million operations, the unit cost of the product should include an element representing one millionth of the cost of the press (less recoverable scrap); this element is the depreciation charge. Exclusion of depreciation from expense will accordingly result in an error in cost of production and in profits just as much as would exclusion of material cost or die cost.

Depreciation, or expiration of service capacity, may arise from several sources. The most commonly indicated source, wear and tear through use, is seldom the governing force. Any force which will result in the withdrawal of a plant item from use is a depreciation factor. The force which results in withdrawal at the earliest date is the governing force in any particular case. Wear and tear is seldom that force since other causes usually operate to cause retirement a considerable time before wear and tear cause such a loss in operating efficiency as to make retirement necessary. Wear and tear always determine maximum capacity of the plant; all other forces tend to reduce the potential capacity and thus the serviceable life. The close

relationship between depreciation and repairs, to be discussed in a later paragraph, illustrates further the place of wear and tear in plant policy.

Two factors other than wear and tear also determine the physical life of plant. These are deterioration and damage or accident. Most plants will deteriorate from mere standing. Rust and rot arise from the action of the elements even when plant is not in use. Accidents may result in irreparable damage. Such accidents may be caused by forces not connected with the plant in question, as hurricanes, floods or explosions. Wear and tear, deterioration and accident may all to some extent be avoided by proper care or remedied by repairs or rebuilding. Avoidance or repair becomes at some point uneconomical because of the action of non-physical forces which makes retirement necessary regardless of material condition. These non-physical forces combine to create a condition of obsolescence.

Obsolescence may be defined as a loss in serviceability due to the action of economic or technological rather than physical forces. It is thus a special case of depreciation. Many conditions will render plant obsolete. Among them are the discovery of new and better ways to do things (new machines or processes), changes in the nature of business (substitution of motor vehicles for horse-drawn), changes in the style and design of product (annual model changes in the automotive industry) and competition (changes in the relative cost of labor and capital which may make new labor saving equipment profitable or may render the present equipment uneconomical). When any one of these conditions arises, the service capacity of the plant in question may become zero and justification for its presence on the balance sheet disappears. The purchase price less any recoverable scrap is a cost of the product already obtained and should have been fully depreciated.

Some authors take the position that depreciation and obsolescence are fundamentally different. The previous discussion is intended to show that this position is untenable, since obsolescence covers an important part but still only part of the causes of loss of service value which we call depreciation. The admitted fact that economic and technological factors are more difficult to estimate does not change the essential character of obsolescence. The physical and non-physical causes of depreciation unite to determine the service life of plant, the factor first requiring retirement being the dominant cause in any given case. In some industries and for certain types of equipment,

wear and tear through use regularly determine service life; in other industries and for other equipment some one of the economic or technological forces resulting in obsolescence is the determining factor. Whatever the cause of retirement, the original cost less recoverable scrap must be charged to the product obtained during the serviceable life; the charge in every case is a depreciation charge.

Various methods have been suggested for handling obsolescence as alternative to including it as an element in the depreciation charge. A list * of such alternatives includes:

1. Recognition of loss as expense when property is eliminated and fact and amount of obsolescence become apparent.
2. Same as (1) except that the loss is charged to net income or surplus.
3. Earmarking of a section of surplus as a reserve for contingencies followed by treatment as in (2).
4. Treating loss as a special deferred charge to be absorbed as early as possible against future revenues.
5. Capitalization of loss as part of cost of property replacing unit eliminated.

Every one of these alternatives is unsound because it fails to recognize that, like physical wear and tear, obsolescence is a factor in cost of production and that provision should accordingly be made to include obsolescence as an expense and a factor in cost. Obsolescence, like depreciation, can seldom be estimated acccurately. At the time of retirement the reserve for depreciation will almost certainly be either too large or too small. The excess or deficiency is a measure of the inaccuracy of the estimate (and of the over- or under-statement) of expense during the serviceable life of the equipment. Correction of the error is always necessary and should be made directly to surplus; if the amount is small the error made by correcting through profit and loss will be small. Except for such corrections of inevitable errors obsolescence cannot be adequately handled, other than by inclusion as an element in the annual expense as a part of depreciation.

The first three of the suggested alternatives at least recognize obsolescence as an expense applicable to prior years by charging it

* Paton, W. A. (ed.), *Accountants' Handbook*, The Ronald Press Company, New York, 1932, p. 605.

off. The last two alternatives are open to particular criticism because the effect of each is to throw the loss forward. A deferred charge which is in reality a deferred loss should never appear on a balance sheet. Losses are properly deductions from the net worth section and as soon as discovered should be subtracted from profit and loss or surplus. The attempt to add such a loss to the cost of new plant overstates the assets and burdens future years with an overstated depreciation charge. The old plant was retired because it was no longer economically serviceable; to add the loss occasioned by obsolescence to new equipment is to add an amount which represents neither real value nor an asset.

The close relationship between repairs and depreciation has already been suggested. Even brief consideration will show that the economic life of equipment is definitely affected by repair policy and vice versa. Where the conditions in an industry are sufficiently stable for obsolescence to become an unimportant factor in determining serviceable life, the useful life can be considerably extended by a careful repair policy. If obsolescence is likely to retire the machine within a short period of time, repairs may be practically avoided in order to work out the machine in a minimum of time. When a serviceable life has been decided upon, it must always be with a definite assumption as to repair policy. All expenditures made thereafter with a view to obtaining the estimated useful life will be repairs, and only expenditures which will increase the length of life or increase the rate of output can be considered as an addition to assets.

Many bases for computing depreciation have been and are used. Theoretically the soundest method is a charge per unit of production. Such rates are used for trucks and tires and in steel plants. The difficulty is to estimate with reasonable accuracy the probable production during the economic life of the equipment. The frequency with which obsolescence rather than wear and tear causes retirement, plus the uncertainties of the business cycle, have led business men to use a time basis as the surest way to completely depreciate the plant cost by the time of its retirement. Uniform production is arbitrarily assumed and the total cost to be amortized is divided by the years of expected useful life to determine annual charge-off as follows:

$$\frac{\text{Original cost less scrap}}{\text{Estimated life}} = \text{rate}$$

The so-called straight line method of depreciation (just described) is open to the objection that the years of bad business are penalized while years of good business are benefited. This can not be avoided except by the use of a production basis. Any attempt to base depreciation on income is unsound because profits and production cannot be expected to show perfect correlation; and because the method would omit depreciation entirely in years in which there were losses.

The straight line method is so generally used as to be almost universal. Other methods have theoretical advantages but practical difficulties. Such methods as the annuity method, the reducing balance method, and the sinking fund method are described in most texts on accounting but are infrequently used. Tables of estimated lives of various kinds of buildings and equipment may be found in engineering and accounting handbooks.

IV. Financial Aspects

Amortization, depletion, depreciation and obsolescence in terms of accounting analysis are all asset decreases offset by expense or net worth decreases.* In the case of amortization, the asset decreased will be Prepaid Interest, Leasehold or other intangible asset; for depletion it will be Mines, Oil Reserves, or other wasting asset; and for depreciation and obsolescence it will be Buildings, Machinery or Equipment. Handled in the simplest possible manner on the balance sheet each would result in a decrease in the appropriate asset account (representing the expiration of prepayment of expense) and a decrease in the surplus section of net worth.* Each asset involved would gradually decrease until it finally disappeared from the balance sheet. This method is generally used in the case of amortization only, while a somewhat different method, to be described in the next paragraphs, is practically universally used to record the effect of depletion, depreciation and obsolescence.

At least four considerations make desirable the saving of original plant cost figures. The first is the fact that depreciation rates are commonly based on original cost so that the retention of cost figures is helpful in determining annual depreciation figures. A second, and

* To the extent that any of the year's production remains in the merchandise inventories the portions of amortization, depletion, depreciation and obsolescence representing cost of that production must be analyzed as asset (inventory) increases.

important, consideration is that if depreciation credits are excluded from the plant account, all other changes in the account will reflect actual changes in the physical volume or capacity of plant. A decrease in the plant account can then be interpreted as an actual excess of retirements over additions and betterments, and an increase can be interpreted as an excess of additions and betterments over retirements. Further, if depreciation credits are segregated it will be possible to consider the adequacy of accumulated depreciation in relation to plant, and finally the fact that depreciation is necessarily an estimate will be emphasized.

For the reasons just outlined, it is usual to segregate the depreciation credits to plant in a separate account, commonly titled "Reserve for Depreciation." Because a portion of the credits to Plant have been so segregated, it is necessary to subtract the Reserve for Depreciation from Plant in order to determine the correct net value (unexpired or unused capacity) of Plant, as follows:

Plant—at cost	$3,649,246.21
Less: Reserve for depreciation	986,435.19
Plant—net	$2,662,811.02

The net figure is identical with the balance of Plant which would be arrived at by crediting depreciation directly to the Plant asset account.

The nature of the Reserve for Depreciation is understood by relatively few persons outside those who have had accounting training. Two important reasons largely explain this misunderstanding. The first is an unfortunate terminology which uses the word "Reserve" to cover several fundamentally distinct concepts, and the second is a tendency to confuse the two aspects of the depreciation transaction with the normal financial effect of including depreciation as an expense item. If the origin of the Reserve for Depreciation is kept in mind its nature will be clear. The Reserve is merely a segregation of a portion of the decreases in Plant; it represents plant which has been consumed in operations, as opposed to plant which has been sold, scrapped or otherwise disposed of. The Reserve for Depreciation is, then, a negative asset, or, better, a deduction from an asset. It has been most aptly likened by one author to the "hole in a doughnut." The area of a cross section of a doughnut is the total

area inside the outer circumference less the area of the hole; the net value of plant is likewise the original cost less the accumulated hole in the asset, the Reserve for Depreciation. Such a hole in an asset cannot possibly be an asset itself, contrary to the more or less popular misconception of the Reserve for Depreciation as cash.

When shown that the Reserve for Depreciation can not be cash, but is rather a deduction from an asset, people are apt to conclude that in such case depreciation is only a bookkeeping manipulation and can be of no interest to any persons other than accountants. This is not true. It is the Depreciation Expense which provides for replacement, not the Reserve for Depreciation. Proprietors of small businesses frequently withhold from the day's sales an amount equal to the cost of goods sold in order to provide for replacing the goods. When the accountant records cost of goods sold as an expense and reduces inventories by the same amount, he does it to indicate that of the sales price (represented by cash or accounts receivable) an amount represented by Cost of Goods Sold is only an exchange of goods for cash (or receivables) and must be kept in the business to replace the goods sold. Unless that amount is retained, the capital has not been maintained. The profit is the excess of goods or claims accepted in exchange over the goods and services given to the purchaser in the sale transaction. Expenses are the values given up in carrying on operations; unless assets acquired through sales at least equal expenses, the enterprise has not maintained its capital, and, as it is commonly expressed, has lost money. Whether the proprietor segregates funds to be used for replacing the goods sold, for replacing the cash spent for wages, and so on, or not, is a matter of financial administration.

Depreciation, included as one of the expense items, assures the retention in the business, if it at least breaks even, of assets equal to the cost value of expired plant. The availability of those assets to meet replacement requirements depends on the use made of the cash and receivables taken in the sales transactions. In the sense, then, that all expenses indicate the necessity of retaining in the business an equal amount of assets, depreciation provides assets of the right amount but not necessarily of the right form to replace expired plant.

Considerable discussion has been focused upon the problem as to whether assets retained in the business through inclusion of depreciation as an expense should be segregated in a replacement fund.

The object of such segregation is assurance of liquid funds for use in replacing plant. This is a financial, not an accounting problem, and its solution depends on understanding normal financial relationships involved. During the early years of any business enterprise replacements will be relatively small. As the years pass, replacements will increase until in a stable business (one which is neither expanding nor liquidating) they will tend to equal in amount the annual depreciation charge. In businesses characterized by a few plant items of large value, annual replacements will not be uniform but are likely to be either very high (when large items are replaced) or very low (in other years). The larger the enterprise and the greater the number of plant items the more nearly uniform will be replacements. Further, no plant is ever maintained in a state of complete newness. Successful operation can be carried on in a plant on which there is accrued depreciation of fifteen to thirty-five or forty per cent of original cost. This is true because the serviceable lives of the different plant items vary. Amounts of accrued depreciation applying to these items range from none for new items to practically one hundred per cent on those about to be retired. During the early years of operation before replacements reach their maximum, a considerable reserve will have been accumulated against all plant. This reserve will reach a maximum and remain approximately constant as soon as annual replacements equal annual depreciation.

The effect of this average replacement experience is that if the policy of setting up a replacement fund is adopted at the inception of the business, the fund will increase (since depreciation will exceed replacements) to a maximum and then remain practically constant as long as the business is stable (since the maximum will be reached at the time replacements equal depreciation, a condition which will continue thereafter unless the business expands further). Thus the net result must be that the average replacement fund is of no use and the segregation of assets in such a fund renders those assets sterile. The normal flow of funds will ordinarily provide for replacements. Only in cases where abnormally heavy replacements require financial planning will a replacement fund be of assistance. In such cases it operates more or less like the tax or vacation clubs formed by banks to assist individuals to meet large periodic payments. We never hear of similar laundry or meat clubs because the amounts are, or should be, within the limits of current income. The object sought from a replacement fund can usually be obtained equally well through

financial budgeting without tying up funds in low-earning assets. The assets retained through depreciation charges in the early years of business operations provide a satisfactory source of funds for expansion since, as has already been pointed out, such funds will never be required for replacement. It is probably safe to consider most of the funds retained through depreciation charges as available for any corporate purpose; the problem is to find the most desirable and profitable use for these and all other funds under the control of the business, regardless of their source.

V. The Economics of Replacements

Much literature is available on the economics of replacements. Investigations by various individuals have resulted in the publication of a number of formulae designed to assist the business man in reaching a sound decision. These formulae are of varying complexity and soundness. Many of the analyses offered by equipment manufacturers are hopelessly inadequate. Business men, and particularly those concerned with plant, naturally approach the question of plant replacement in a state of bewilderment as to which of the many formulae and analyses they can accept as satisfactory. It is not the object of this paper to add to the present confusion by suggesting a new formula. Rather it is the object to point the way to such fundamentals as will simplify what has been made unduly complex.

Perhaps the most common error in comparing equipment or processes is to fail to make the comparison on similar tasks. The assumption is frequently made, often unconsciously, that the total output of two machines of varying capacities can be used. This is certain to lead to unfortunate results. Comparison should always be made upon the basis of the production required, and that production must be identical for the two alternative methods under consideration. This assumption will usually mean either considerable unused capacity under one method or else two or more units under the other method. Savings in running time per unit or operation do not result in savings in cost unless the added production possible can be used or unless operators can be shifted to other tasks (or laid off) as soon as the required production has been obtained. In every case, total annual costs must be charged to the production of the period; if the machine is idle half the time, then the busy half must bear the total costs. Desired production is the first essential figure in any comparison.

The mistake described in the previous paragraph is always made easier by attempts to make the comparison on the basis of unit costs. Conversely the use of annual costs of required production will avoid this and other errors. There is no fundamental error in the use of unit costs for a careful analyst can arrive at sound conclusions in this way. The reasoning is difficult, however, and the adjustments more delicate. The use of annual costs for usable output is a desirable insurance against mistakes.

A real error, and a common one, lies in the assumption that certain expenses will be the same under both methods. The most usual example of this is the use of the same burden rate for both machines or methods. Since the object of the analysis is to measure the difference in cost, no error will be involved if common expenses are omitted from the calculations. The trouble is that expenses which we assume to be common have an unfortunate habit of differing. Even material cost may differ because of variations in waste or spoilage. Labor costs obviously differ, for the basis of cost reduction usually lies in the saving of labor. Burden also will vary in most cases, for there are differences in taxes, insurance, depreciation, power, space requirements, repairs, supplies and even supervision. Burden rates are apt to be average rates for a whole department and may not be accurate for even the old machine. Every item of expense must be considered in detail to determine the effect of the new equipment or method. Much grief would be avoided if the attitude were always taken that no expenses would be common in amount.

The word "saving" is subject to misinterpretation. The popular confusion between saving and reduction of cash outlay should not bother trained engineers. A reduction in current cash outlay may be more than offset by increased depreciation or other non-cash expense. A saving exists when there is an increase in net worth resulting from the adoption of the new method. Unless net worth (the owner's interest in the business) increases, apparently favorable changes in cash or any other asset or liability are not accompanied by real savings. Any analytical comparison of two machines, methods or processes must, therefore, seek to measure the effect of various choices on profits and net worth. The importance of this ideal will be more apparent in a later paragraph.

The substitution of a new machine or method for an existing one must depend on the relation of resulting savings to the added investment required, rather than either to the total cost of new equipment or

to that plus the loss on the old. If the savings constitute an adequate return on the added investment, the purchase is desirable and the mere fact that this saving does not constitute an adequate return on the total cost, or the total cost plus the loss on the old equipment, is no reason not to make the purchase. The investment in old equipment is a sunk cost to which the enterprise is committed. New equipment should not be burdened with a requirement of earning a return on past mistakes. If the old equipment can be used for partial payment on the new either by sale or exchange, then the amount of investment necessary to accomplish the desired saving is correspondingly reduced and the change becomes increasingly attractive. Where the comparison is between present hand methods and a choice of new methods involving the purchase of equipment, the saving accomplished by the least expensive equipment must of course be related to the entire cost of that equipment; the additional saving resulting from more expensive equipment must be measured against the additional investment required.

Reference has already been made to the many formulae developed as an aid in deciding when new methods or equipment are desirable. An objection to all of these formulae is that certain definitions and terms are assumed and used, and unless the formula is solved with those definitions and terms in mind, erroneous results may follow. There is also a tendency on the part of the user to displace judgment with mathematics, which is never satisfactory. Further, the derivation of many of these formulae involves mathematical processes beyond the understanding of the layman, so that the soundness of the formula must be accepted on somebody's say-so. Such formulae are therefore dangerous in the hands of the average business man. A real understanding of the basic principles involved plus an analytical attitude will produce correct results without the necessity of advanced mathematics.

Most of us are familiar with comparative balance sheets and income statements. The same simple arrangement can be used in the comparison of equipment. Exhibit I illustrates an arrangement that might be used. The object of this tabulation is to guard against the errors discussed in previous paragraphs. It therefore begins with a statement of the estimated required average annual output in units. Expenses are itemized and entered as estimated average annual expenses. The final figure is the rate of savings to the additional investment required. Real difficulty will exist in esti-

mating average production and the expenses involved in that production. Many of the expenses will, of course, be fixed regardless of the rate of production, but others will vary. The tendency of repairs to increase as time passes must be taken into consideration.

Many business men purchase equipment only when it will pay for itself within a definite and usually short period. The determination of the period within which equipment will pay for itself is of interest to such individuals. The problem is simple as soon as it is realized that the period is the number of years it will take the net savings, before including provision for depreciation on the new equipment, to amount to the additional investment required. A simple modification of the "Comparison of Equipment" will provide the answer. This tabulation is shown as Exhibit II. The variations from Exhibit I are (1) the omission of provision for depreciation on the new equipment, (2) the inclusion of interest at six per cent on the average investment in each equipment, and (3) the substitution of "Net Savings after providing for interest but without providing for depreciation on the new equipment" for "Net Savings" in the earlier arrangement. Interest is included because the savings should provide an interest return on the investment in addition to return of the investment. Interest is computed on a base of one-half of the present cash value of each equipment since that is the average investment during the use of the equipment. The net savings figure determined in Exhibit I fits the definition of savings, but the modifications in Exhibit II are necessary to compute the time required for the new equipment to return out of savings the additional investment required.

An important element of expense and therefore of savings is depreciation. Adequate treatment of this item is essential to a sound comparison of methods or machines. In the tabulation shown as Exhibit I, depreciation has been included but is based on the present cash value of each equipment. The equipment, the replacement of which is under consideration, will be carried among the plant items at a book value determined by deducting accrued depreciation applicable to this equipment from its original cost. Only by chance will this book value coincide with the second hand or cash value of such equipment. Much discussion and many mistakes have centered on the choice of base upon which the depreciation figure used in the comparative analysis is to be computed. The use of both book and

COMPARISON OF EQUIPMENT

		OLD EQUIPMENT	NEW EQUIPMENT
(1)	Estimated required average annual output*(in units)		
	Estimated average annual expenses		
	A. *Machine Cost*		
(2)	Depreciation**	$	$
(3)	Taxes		
(4)	Insurance		
(5)	Maintenance and repairs		
(6)	Power		
(7)	Space cost (rental charge)		
(8)	Supplies		
(9)	B. *Direct Labor Cost*		
(10)	C. *Material Cost*		
	D. *Other Costs* (itemize)		
(11)	Special tools		
(12)	Indirect labor		
(13)			
(14)			
(15)	TOTAL EXPENSES	$	$
	NET SAVINGS		
(16)	New over old		$
(17)	Old over new (in red)	$	
(18)	Total installed cost new equipment		$
(19)	*Less:* Allowance on old equipment		
(20)	ADDITIONAL INVESTMENT		$
(21)	% NET SAVINGS TO ADDITIONAL INVESTMENT (16) ÷ (20)		%

* Must be identical for both equipments.

** Based in each case on *present cash value* and estimated probable useful life

EXHIBIT I

DETERMINATION OF PERIOD DURING WHICH NEW EQUIPMENT WILL PAY FOR ITSELF

		OLD EQUIPMENT	NEW EQUIPMENT
(1)	Estimated required average annual output*(in units)		
	Estimated average annual expenses		
	A. *Machine Cost*		
(2)	Depreciation**	$	$ xxxx
(3)	Taxes		
(4)	Insurance		
(5)	Maintenance and repairs		
(6)	Power		
(7)	Space cost (rental charge)		
(8)	Supplies		
(9)	B. *Direct Labor Cost*		
(10)	C. *Material Cost*		
	D. *Other Costs* (itemize)		
(11)	Special tools		
(12)	Indirect labor		
(13)			
(14)			
(15)	TOTAL EXPENSES (exclusive of depreciation on new equipment)	$	$
(16)	INTEREST @ 6% (on one-half present cash value of each equipment)		
(17)	NET SAVINGS (Providing for interest on average investment but omitting depreciation on new equipment)		$
(18)	Total installed cost new equipment		$
(19)	NUMBER OF YEARS required for new equipment to pay for itself out of savings		
	TOTAL INSTALLED COST / NET SAVINGS (line 17 above)		yrs.

* Must be identical for both equipments.
** Based on *present cash value* and estimated probable useful life.

EXHIBIT II

present cash values has been advocated and the use of either will lead to sound conclusions provided there is a proper accompanying treatment of other items. The use of present cash values as the depreciation base for both the old and the new equipment was chosen for reasons to be presently outlined. Of course for the new equipment the present cash value, the installed cost and the book value are identical. For the old, however, the book and present cash values will differ for the reason that depreciation rates are determined to write the original cost down to the second hand or scrap value at the estimated time of retirement; retirement at any time in advance of that date is proof that the original estimate of serviceable life was in error and will usually find the book value in excess of the then cash value. Consequently disposal of the equipment will involve a write-down because of unexpected obsolescence. The treatment of this write-down in the comparison has caused the difficulties. Obviously the cost reductions (including the annual depreciation charge) resulting from the new equipment must be large enough to offset this necessary write-down, for it is the size of the savings which renders the old machine obsolete and decreases its value more rapidly than would have been the case had the new equipment not been developed. Provision for absorption of the write-down will be accomplished by the use of a depreciation figure which is based on the cash value of the old equipment at the time of substitution, while the use of a depreciation figure which has been based on book value will fail to make such provision.*

Where considerable amounts are involved and the analysis is for equipment of varying useful lives, the effect of the compounding of interest can be highly significant in the result. For the short periods during which the business man expects equipment to pay for itself, however, compound interest may be safely neglected unless there is a very wide difference in required investment under the methods being considered. For this reason and as an added factor in producing simplicity, compound interest has not been taken into consideration in either Exhibit I or Exhibit II.

Perhaps no better way can be found of showing the absurdities which have entered into the analysis of savings resulting from replacements than to consider a typical analysis. The "Replacement Profit Estimate" reproduced as Exhibit III was included by

* An illustrative case showing why this is true is included in Appendix A.

a machine tool maker as an integral part of an advertisement in which the reader was urged to "send specifications of . . . gears" in order that the maker might submit "conservative production and replacement profit estimates presenting the savings possible." Consider the conservative nature of the estimate! No mention is made of required production but a machine which is expected to produce

REPLACEMENT PROFIT ESTIMATE

FOR- BLANK CORPORATION

KIND OF GEARS- SPIRAL BEVEL GEAR 41 Teeth—4.373 Dia. Pitch—1¼"Face

MACHINE RECOMMENDED- No. 16 Spiral Bevel Gear Generator

INVESTMENT REQUIRED- $6700.00 (Approx.)

COMPUTATION OF SAVINGS-

Present time each-	24.0	Minutes
Proposed time each-	12.4	Minutes
SAVING EACH-	11.6	Minutes

$$\text{SAVING EACH-} \quad \frac{\text{Saving in Minutes} \times \text{Hourly Rate}}{\text{Minutes per Hour}} = \frac{11.6 \times 2.00}{60} = \$0.39$$

ANNUAL SAVING-

Days per year	Hours per day	Minutes per hour	Efficiency factor	Saving per piece	
250	x 16	x 60	x .80	x .39	
12.4 (Proposed Time Each)					= $6038.71

GROSS ANNUAL SAVING-	= $6038.71
Less- 10% Depreciation on Investment	= 670.00
NET SAVING PER YEAR	= $5368.71

$$\frac{\text{NET SAVING PER YEAR}}{\text{INVESTMENT REQUIRED}} = \frac{\$5368.71}{\$6700.00} = 80\% \text{ ANNUAL RETURN ON INVESTMENT.}$$

EXHIBIT III

a finished piece in hardly more than half the time required by the present equipment is assumed to be fully occupied. Unless two of the present machines are in almost constant use or unless production is about to be almost doubled the new machine will be idle very nearly fifty per cent of the time and the total overhead attaching to it must be prorated over only fifty per cent of capacity hours. The hourly rate given must be based on present costs and hours, for every hour saved is supposed to mean $2.00 saved. What are the savings? Overhead costs, which if not charged to the product will appear as unabsorbed burden due to idle time. Such "savings" will decrease profits, not increase them. But the $2.00 rate is probably not even correct on a capacity hour basis. It must include direct labor to avoid an almost unbelievable mistake. Will the new machine be run by an operative paid the same rate? The use of the rate assumes identical wage rates and identical burden items. If this condition really exists then the result will be buying a new machine which is to be worked half the time at double the rate (in order to take care of idle time). Burden items cannot be expected to be identical. Power requirements will probably be greater in order to remove the same quantity of metal in a considerably shorter time. Further, if the present rate is soundly determined and really applies, it must contain provision for depreciation; in such case the deduction of $670.00 for depreciation constitutes double provision. It is impossible to unravel the tangle for lack of information, but the "conservative" estimate is probably over double the real saving, and very possibly there may be no saving at all. A $6,700.00 additional investment would involve a $400.00 a year interest cost which added to the manufacturer's own estimate of added depreciation would very nearly eat up any possible saving in labor.

VI. Summary

Recent industrial and economic developments have forced reconsideration of equipment policies. Basic to an intelligent approach to such policies is an understanding of the effect of equipment upon costs. All expenditures for equipment must be recognized as prepaid expenses representing services to be performed in the obtaining of future product. Accordingly provision must be made for including a proper portion of such outlays in determining the costs of product benefiting. Amortization, depletion and depreciation are all

expense items having for their object the making of such provision. They differ only in the type of assets to which they apply; amortization applying to intangible prepaid items such as insurance; depletion to wasting natural assets; and depreciation to buildings, machinery and equipment. Like other expenses they serve to keep in the business assets acquired in sales transactions equivalent to assets consumed in operations. While many advocate the segregation in a special replacement fund of assets retained by charging depreciation, this should be recognized as a question of financial policy. Such segregation not only is usually unnecessary but also results actually in withdrawing assets permanently from earning power. In the replacement of equipment careful analysis is needed to determine the reality of supposed savings claimed by machinery salesmen. The use of complicated formulae is unnecessary. Simple tabulation plus intelligence will assure sound results.

APPENDIX A.

Case illustrating effect of substitution of equipment

A. *Assumptions*

I. Condensed balance sheet at time of proposed substitution.

Current assets	$150,000	Current liabilities	$ 50,000
Plant	100,000	Net worth	200,000
	$250,000		$250,000

II. Data on present plant.

Book value	$100,000
Cash value	$ 25,000
Estimated life	5 years
Final scrap value	none
Total annual operating expenses exclusive of depreciation	$100,000

III. Date on proposed equipment.

Installed cost	$150,000
Estimated life	10 years
Final scrap value	none
Total annual operating expenses exclusive of depreciation	$ 90,000

IV. Gross annual income $120,000.

B. *Analysis of savings*

I. Basing depreciation of old equipment on *cash value.*

Expenses	*Old*	*New*
Depreciation	$5,000	$15,000
Other operating expenses	100,000	90,000
	$105,000	$105,000

Net saving.....neither gain nor loss

II. Basing depreciation of old equipment on *book value.*

Expenses	*Old*	*New*
Depreciation	$20,000	$15,000
Other operating expenses	100,000	90,000
	$120,000	$105,000
Net saving—new over old		$15,000
Total installed cost of new equipment		$150,000
Less: Allowance on old equipment		25,000
Additional investment		$125,000
% Net saving to additional investment		12½%

C. *Comparison of effects of retention and substitution on balance sheet.*

I. Effect of retention for five years.

	BEGINNING BALANCE SHEET		DEBIT	CREDIT	FINAL BALANCE SHEET	
Current assets	$150,000		(*b*) $600,000	(*d*) $500,000	$250,000	
Plant	100,000			(*a*) 75,000 (*c*) 25,000		
Current liabilities		$50,000				$50,000
Net worth		200,000	(*a*) 75,000 (*c*) 25,000 (*d*) 500,000	(*b*) 600,000		200,000
	$250,000	$250,000			$250,000	$250,000

(*a*) Write down of old machine
(*b*) Gross income (5 years @ $120,000)
(*c*) Depreciation (5 years @ $5,000)
(*d*) Other expenses (5 years @ $100,000)

Balance sheet at end of five years

Current assets	$250,000	Current liabilities	$50,000
		Net worth	200,000
	$250,000		$250,000

II. Effect of substitution over five year period.

	BEGINNING BALANCE SHEET		DEBIT	CREDIT	FINAL BALANCE SHEET	
Current assets	$150,000		(a) $25,000 (c) 600,000	(b) $150,000 (e) 450,000	$175,000	
Plant	100,000		(b) 150,000	(d) 75,000 (a) 100,000	75,000	
Current liabilities		$50,000				$50,000
Net worth		200,000	(a) 75,000 (d) 75,000 (e) 450,000	(c) 600,000		200,000
	$250,000	$250,000			$250,000	$250,000

(a) Sale of old machine
(b) Purchase of new machine
(c) Gross income (5 years @ $120,000)
(d) Depreciation (5 years @ $15,000)
(e) Other expenses (5 years @ $90,000)

Balance Sheet at End of Five Years

Current assets	$175,000	Current liabilities	$50,000
Plant	75,000	Net worth	200,000
	$250,000		$250,000

III. Effect of retention for various periods.

Balance Sheets at the End of Various Periods*

	1 YEAR	3 YEARS	5 YEARS	10 YEARS
Current assets	$170,000	$210,000	$250,000	Old equipment retired at end of five years and must be replaced by similar or other machine.
Plant	20,000	10,000		
Total assets	$190,000	$220,000	$250,000	
Current liabilities	$50,000	$50,000	$50,000	
Net worth	140,000	170,000	200,000	
Total liabilities	$190,000	$220,000	$250,000	

* Determined as in I and II above.

IV. Effect of substitution for various periods.

Balance Sheets at the End of Various Periods*

	1 YEAR	3 YEARS	5 YEARS	10 YEARS
Current assets	$55,000	$115,000	$175,000	$325,000
Plant	135,000	105,000	75,000	
Total assets	$190,000	$220,000	$250,000	$325,000
Current liabilities	$50,000	$50,000	$50,000	$50,000
Net worth	140,000	170,000	200,000	275,000
Total liabilities	$190,000	$220,000	$250,000	$325,000

* Determined as in I and II above.

Comment on Effects of Retention and Substitution

The results of the analyses in BI and BII above were that in the analysis in which depreciation was figured on the basis of cash value there was no saving (nor any loss) resulting from the substitution of the new equipment; it was therefore a matter of financial indifference whether the old machine was retained or the new one substituted. The other analysis, in which book value was the basis, showed an apparent saving. Consideration of the effects of retention and substitution on the balance sheet (CI, CII, CIII and CIV above) shows the net worth item to be identical under either hypothesis at the end of any period.* This equality of the net worth item shows clearly the fact of neither loss nor gain and supports the use of cash value as a basis for computing depreciation on the old equipment as far as the comparison is concerned. At the same time, however, the net worth in each case increases from year to year by a constant amount, $15,000. Total costs (including both depreciation and other operating expenses) appear as $105,000 for both machines under analysis BI, while the assumed gross income is $120,000; hence an annual income of $15,000 will appear on the operating statement if the new machine is substituted, or if the old machine is written down to cash value (which it would not be). Total expenses for the old machine in BII (where book value was used) were $120,000, so that the operating statement would show no profits; but the same profit of $15,000 appears for the new machine and is shown in the analysis as a net saving. Careful consideration will show the $15,000 item to be a legitimate profit on the annual operating statement, but not to be a saving. This is true because if the old machine is discarded the loss due to write-down must be taken as a cost of prior production, while annual operating costs (including depreciation) will be reduced by the substitution; if the gross income remains the same there will be a profit on the operating statement. Until sufficient time has passed, however, for the annual profits to equal the write-down there is no saving in the sense of improved net worth, for while the write-down must be taken immediately as a cost of past production if the old machine is discarded, the whole book value (assuming no ultimate

* Net worth is identical at all times from the start only if the write-down to cash value is taken immediately in both cases. Otherwise, the net worth under the assumption of retention will remain constant at $200,000.00 while five years (the remaining life of the old equipment) must pass before the net worth under the assumption of substitution reaches $200,000. The reason for this will appear in the text above. Of course if the old equipment is kept, the write-down will not be made; regular depreciation will continue.

scrap value) will be treated as a cost of future production if it is retained. The use of cash value as a basis for depreciation in the analysis decreases the annual costs of the old machine by an amount equal to a proration of the difference between book and cash values of the old machine over its remaining life. It thus requires the costs under the substitute plan to be decreased by the same amount before any saving appears.

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Discussion

W. P. Fiske (preceding paper) : I am certainly happy to be here, and for two reasons. In the first place, I feel particularly pleased that you gentlemen are interested enough in this subject, which is not a direct part of your own field, to include it as a part of your program. The presence of this topic on your program is an indication of the breadth which must be present in any good engineer or in any good member of any particular profession. I am further pleased to be here because I am an outsider, and not only am I an outsider but I am a member of that now somewhat notorious profession of College Professors. I even had to come through Washington in order to get down here, but I am, perhaps, one of the few college professors who is still teaching school.

The subject I have to take up today is of extreme importance to anyone concerned in any capacity with either public or private enterprise. There is no business which can be without depreciation in some form and, seriously, there is no subject of a financial, accounting or business nature which is more worthy of your time and thought than this subject of depreciation. Although the title of my paper is very long and includes several other terms, the primary object of the paper is to discuss Depreciation. The latest publicity given depreciation was a suggestion by the Taxation Board in Washington that for the coming year all depreciation allowances be reduced twenty-five per cent. As though it could be done as easily as all that. Now my object here today is not to read my paper, but rather to promote some discussion, and if I can possibly correct a few common misconceptions I shall feel well rewarded.

CHAIRMAN DORR: Gentlemen, the subject is open for discussion.

C. R. DELONG: Professor Fiske, I understand certain industrial and commercial concerns make a practice of carrying their depreciation charges in line with general business conditions. That is, in lean years, taking less probably than normal depreciation, and in good business years taking more than normal depreciation. What are your ideas on that subject?

W. P. FISKE: In the first place I purposely omitted anything more than mere mention of it at the termination of the section on depreciation in this paper, because I believe it is a technical subject which you can find better discussed in the technical literature of the field. But the feeling that the business man has in that case is not only based upon the desire to make money in bad periods, but also upon an honest business fact, and that is that if we take this cost, representing a certain capacity, we will say 100,000 miles for our truck, in this illustration, that if we use that 40,000 miles in one year, and 60,000 miles the next, because the first year is not quite as good as the second, that the business man is quite right in feeling that the second year should have higher depreciation charged to it than the first year. Now the difficulty with that policy is of two types: in the first place, because of the impossibility of forecasting economic conditions we cannot forecast the use we are going to get out of a machine. Nor can we place that use in particular years. Yet we have to get that cost into our income statements by the time the machine is retired if we do not want to be out of pocket. Therefore, the business man says—if we cannot guess the output we will at least guess the years, and it does not make any difference whether we are going to use it or not, we are going to write it off. That is a conservative thing to do, and there is justification for the so-called straight line method, which involves the operation of equal use in each equal period. The other difficulty is that the business man is always willing to think of these things in bad years but never thinks of them in good years. When prices are going up the business man never tells the stockholders that the majority of the profits that

he is making are due to the fact that he is selling his inventory at increased prices; he just pats himself on the back and says, "Well, look at the money we are making." But what happens when prices start to go down? He takes and sets out in inventory, losses due to change in prices and says, "This was not our fault" and puts that in big figures. Now, the business man is willing to cut depreciation in bad years, but the average man likes to forget about it in good years, so that we have arrived at the conclusion that the safest thing to do is to take a like amount every year, and then we will certainly come out right. For that reason, in the majority of cases at least, I think the current practice is correct. I would like to point out, however, that in the case of trucks, tires, steel business, so-called production rates are in use and that the use of those production rates does result in varying depreciation in good years and bad years. Does that answer your question?

C. R. DeLong: Yes, thank you.

A. E. Marshall: There are two questions I should like to ask Professor Fiske. I will ask them separately. Based on reading the paper, if it is proper to include the cost of forms for concrete construction in the cost of buildings, why is it not equally sound to add the residual undepreciated balance sheet values of equipment rendered obsolete through advances in the arts, to the cost of the new replacing equipment?

W. P. Fiske: If we are going to build a concrete building, a part of the realized cost of getting that finished concrete building in the construction of certain forms in which the concrete is poured, which are later removed, we cannot get that building without making that expenditure. That is not quite analogous to the inclusion of the undepreciated value of the machines as part of the cost of the new machine. It would be more analogous if we attempted to put up a shack which was wholly inadequate, used it for awhile, found out it was inadequate and then said, "Just because we have not written it all off, we will add what is left to the cost of the new building."

To include the undepreciated costs as part of the cost of new equipment is equivalent to saying that the cost of past mistakes is part of the cost of present equipment. If you get this concept of an asset as a prepaid expense clearly in your mind, you will realize that to include in the undepreciated portion of this article in the cost of the new equipment is equivalent to saying that that cost is a cost of benefits still to be received, which it is not. Only the cost of the new equipment is the cost of benefit yet to be received, everything else is something that is in the past. It is water over the dam. It never does any good to put an item on the balance sheet, "deferred charges to operations," which consists of losses, because if the banker gets hold of that balance sheet he will draw a blue pencil through that particular item immediately, and is likely to draw the conclusion that you will do the same thing everywhere else and proceed to mark everything else down.

It seems to me the only way to approach that accounting problem is to approach it with the determination that we are to present the facts as they are. It is only by doing that that the business man can have the information which he needs to solve his problems correctly.

We will take this Commercial Solvents case. If the problem of replacing that plant comes up, it will only be by digging back through the files that that company will be able to get information with the help of which they can make a reasonable comparison between present equipment and the suggested equipment. If they reduce the cost of the present equipment by writing it down, it will look as though it is more economical than it really is. Does that answer your question?

A. E. MARSHALL: Yes, thank you.

S. D. KIRKPATRICK: Some years ago I heard a lecture on chemical engineering economics by one of our distinguished chemical engineering members now helping to run the Government. At that time he was Professor of Chemical Engineering at a small school up in New England. As I recall that lecture, he said about all the economics a chemical engineer needed to know were the laws of compound interest. I wonder if Professor Fiske would care to elaborate and tell us how the factor of compound interest determines the choice or selection of equipment?

W. P. FISKE: I think every engineer should know about compound interest, but I am afraid I do not agree that it is the only thing —I think it is the last thing he should know. We all know that a dollar to be received ten years from now is not worth as much as a dollar to be received today. If we have some equipment to buy and it involves a present downpayment on the one hand, and we have as an alternative the leasing of the same equipment for a certain yearly charge, the only way we can make a real comparison is to determine what is the present value of those future expenditures for comparison with the present value of the outlay.

Where large amounts are involved and where considerable periods of time are involved, compound interest can make a very great difference. In the problem of replacement, however, the average business man has rather high standards as to the time within which the equipment must pay for itself; he does not want to buy equipment unless it will pay for itself, we will say, within two or three years, or something of that kind, so that unless there is a very wide variation between the amounts to be invested under the two alternatives, the difference resulting in the case of such a short period would be slight. I think for that reason, in the majority of cases, we can forget about compound interest, particularly if you realize that the factor of error in estimating, first, the life, and secondly, the ultimate resale value, is far greater than is the compound interest factor. We are dealing with statistical figures and do not want to make the mistake many statisticians make of taking figures only correct within fifteen or twenty per

cent and then carrying their method of analysis down to two or three decimal points. The figures do not justify that, and in the majority of cases I do not believe the replacement charges justify the item of compound interest. It should be recognizable as a factor, however. Does that answer your question?

S. D. KIRKPATRICK: Yes.

A. E. MARSHALL: The second question I have has no direct bearing on the paper. Frequently, one finds on the assets side of a balance sheet of chemical manufacturing companies, under the heading of patents, sums which are obviously larger than the total overall constituted by purchasing, developing and securing patents owned by the company. Patents have a monopolistic life fixed by governmental grant to the patentee and except in a few cases, a much shorter actual life resulting from the discovery by others of improved processes or equipment, which makes the company's patents of less, or even zero, value. How should patents be set up on the assets side of a balance sheet, and what method should be followed in depreciating this form of asset?

W. P. FISKE: Patents are no different in respect to valuation than any other of these productive assets. If the primary object of our accounting is to state facts and to determine profits correctly, we believe that the best single method of valuing productive assets is cost, because the use of that cost figure results in the proration of the actual cost of the service received over the periods that are benefited and in that way can arrive at a reasonably correct figure of profits.

In the valuation of patents, the normal rule is that patents should not be valued in excess of what is paid for them. That means, in many cases, the cost of development and the cost of acquiring the patent. In other cases, where the patent is purchased from an outside party, regardless of what it cost the original inventory, the cost to the company which has the patent is what they paid for it. That is perfectly legitimate. Writing up the asset, patents, is open to all the objections of writing up any of the assets; that is, it amounts to an anticipation of profits and further results in a misleading cost figure, if you carry it through to its logical conclusion.

Now if we have the patents on the books at a fair cost value, the remaining problem is the problem of prorating. And, again, just as the physical wear and tear and the decline in engineering efficiency determines the maximum period of use in the case of equipment, so the governmental time limitation determines the maximum period of benefit from the patent. But patents may become obsolete just as may equipment, and our job is to make the best guess we can as to how long it will be useful and prorate it over that period, regardless of how long it may have actual legal value.

CHAIRMAN DORR: Professor Fiske, in case you have spent a lot of money on a patent so that it has cost you a great deal at the time you use it, would you charge it at the lower price?

W. P. FISKE: I would. It is a mistake of the past, and I cannot see where there is any more justification for putting it on the books at a value which we cannot get back than there would be in paying a price for a piece of equipment which we realize would cause us to lose money on every product that came from it.

CHAIRMAN DORR: So that you would charge it at the cost or estimated value, whichever was lower?

W. P. FISKE: Yes, I think mistakes should always be recognized as soon as they become probable and should be provided for.

CHAIRMAN DORR: Are there any further questions?

C. R. DELONG: One more question, please. With reference to writing down plant assets, I happen to know of a company a year and a half or two years ago that looked at their physical plant assets and said, "We have some plants built during wartime at high cost; we have some others built in 1928 and 1929 at high construction costs." They adopted the policy of revaluing those plant assets at present replacement costs, and went back and put that value on their books and then depreciated that value over the period these plants had been in operation at normal rates, and the net result of that is that they effected a saving in annual depreciation charges, some of them by half a million dollars. I would like to get your idea on that.

W. P. FISKE: The arguments for write-down which have appeared in the last two or three years were of three types. In the first case we have had cases where capacities had been built up to away beyond any probable needs. We made a mistake in buying something we could not use. Now, our common sense tells us when we have done that the best thing to do is to get rid of it. That equipment should be segregated in the normal case and written down to what we can hope to get for it and taken out of cost figures.

The second case is obsolescence due to the development of the art and due to the fact that with this long period of low production, the possibility of ever getting our expected production out of the machine has become pretty small. Then again, there is the case of past loss which should be written off.

Now there is nothing unusual about those two write-downs, except that business men decided all of a sudden that they were going to do it, and their need for improving their income statements brought them to the realization that that was a good thing to do.

The third argument is the argument of a radical change in the price level. Now, the price level is the one problem that, so far as I know, has the accountants beaten. I know of no real comprehensive plan of recognizing changes in the price level. Every time we buy a new piece of equipment or a new piece of material, the changes in the price level are reflected so that the values on our balance sheet are conglomerate of the values that existed at the time we bought our oldest piece of equipment and the present values now covering them. If we have a very radical change in the price level, either up or down,

it may have a marked competitive effect upon an industry. If you find that your competitors are building new plants at very low prices, or buying bankrupt estates—and some one remarked at one time that what we needed was not bankruptcies but a few more fires, because a bankrupt plant reappears again at a lower price—then your costs will be so high in many cases as to put you at a severe competitive disadvantage.

There is no need of carrying that millstone around your neck for the rest of your life. It will hurt the morale of your organization because they will see they are losing money when they know they are doing a good job, and under those circumstances if it is apparent that the decline in price level will continue as a permanent factor for the balance of the life of the equipment, I believe that those write-downs are justified. But that is far different from taking the attitude that we are just going to clean the thing off. In that case the object is to practically reorganize the company upon the new and lower price level and to go ahead in fair competition with the others in the field.

CHAIRMAN DORR: There is one other matter and that is the question of expected taxation that sometimes determines the amount of depreciation one takes.

W. P. FISKE: Yes, and that of course may possibly be a factor in write-down.

CHAIRMAN DORR: Is there any other discussion? If not, I know I express the feeling of the meeting in giving the greatest possible appreciation and thanks to Professor Fiske for coming here as a visitor and giving this most excellent paper. The question of accounting sometimes has been carried to excess, and occasionally, has gone the other way. I had a friend visiting a factory in Czechoslovakia some years ago, and in talking to the owner he remarked that he did not keep accounts, simply a check book. Well, the factory looked prosperous and good and my friend said, "Well, how can you possibly tell whether you are making money or not?" "See that umbrella over in the corner" asked the owner? "Well, five years ago that was all I owned. Now I own a factory." There was no argument about it.

Next we will have a paper on "Recent Developments in Nitrogen Fertilizers" by Mr. C. L. Burdick, Assistant Chemical Director of the Ammonia Department of the duPont Company. I think that the nitrogen industry is one in which the experience of obsolescence must have come home to many people, including our friends in Chile. Mr. Burdick.

RECENT DEVELOPMENTS IN NITROGEN FERTILIZERS

By C. L. BURDICK*

I. *General:*

The synthetic ammonia industry is approaching the twentieth anniversary of its large scale commercial development. In the early years of this century fears were regularly expressed regarding prospective shortage of nitrogen. For the last fifteen years the pressure has been steadily for cheaper nitrogen:

In 1925 the du Pont Company embarked on the fixation of nitrogen by the synthetic ammonia process to safeguard and assure its supplies of ammonia and nitric acid for explosives and other industrial uses. In 1928 du Pont, with a plant capacity beyond peacetime or war-time requirements for nitrogen, necessarily turned attention to the possibility of finding outlets in the fertilizer field. The following figures disclose the pertinent facts regarding the present nitrogen situation in the United States.

The U. S. War Department's estimate for the military demand for fixed nitrogen for explosives for a first-class war would be not to exceed 150,000 tons of nitrogen per year.

The production capacity for inorganic nitrogen compounds for the United States is approximately:

TABLE I

	Annual Productive Capacity in Short Tons of Nitrogen
By-product sulfate and by-product ammonia.....	190,000
Synthetic ammonia plants	300,000
Total	490,000
Of which not to exceed.....	140,000 tons
Will satisfy any prospective industrial demand for some time to come which leaves.....	350,000 tons
Of fixed inorganic nitrogen available for other than industrial uses which means naturally *fertilizers.*	

In addition to this 350,000 tons of inorganic nitrogen available for fertilizers some 50,000 tons of nitrogen in the form of organic ma-

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terials such as cottonseed meal, fish scrap, tankage, etc., finds a place in the fertilizer market. This makes a total of 400,000 tons of nitrogen for fertilizer purposes available from domestic sources. The rate of consumption of fertilizer nitrogen in 1929 (which represents a high average figure) was 365,000 tons of nitrogen in all forms according to Brand.[1]

It is, therefore, evident that for either peace-time or war-time conditions the nitrogen industry has to depend in large measure on agriculture for its markets, and further that in a state of emergency the war-time military requirements plus maintenance of normal industrial demand would still leave available large quantities of domestic nitrogen available for fertilizer purposes.

Six years ago the Ammonia Department of the du Pont Company began a careful survey of fertilizer technology as concerns applicability of nitrogen. Nitrogen has in the past been an expensive fertilizer ingredient and there has been obvious need for cheaper superior nitrogen fertilizers. The advent of the method of treating superphosphate or mixed fertilizers with free ammonia indicated there were possibilities ahead for a newer technology involving nitrogen on the basis of cheaply available domestic supplies of synthetic ammonia.

Many possible nitrogen compounds were considered and many methods of processing of nitrogen with phosphoric acid and potash were studied. The general conclusion reached was that the treatment of superphosphate with anhydrous ammonia should basically be the cheapest manner in which synthetic nitrogen can be added to any fertilizer material. Synthetic urea appeared to be next in line to offer the best prospects for marketing nitrogen in an economical and efficient form. Experimental and technical study of the urea synthesis was accordingly undertaken. Manufacture of a combination urea-ammonia liquor for ammoniation of mixed fertilizer was begun roughly one and one-half years ago and a wide manufacturing and agricultural experience with it has since been obtained.

II. *History and Background Concerning Urea:*

Crude urea is one of the oldest materials used for fertilizer purposes. In the form of "Liquid Manure," it has probably been employed since agriculture first began.

The large scale advent of synthetic urea in Europe some thirteen

years ago, stimulated a large amount of experimental and practical field work to evaluate the efficiency of urea in comparison with other standard fertilizer nitrogen substances. A great deal of work has been done in this country by state agricultural experiment stations and the U. S. Dept. of Agriculture. Results of this work show urea to be, from both the experimental and practical viewpoint, a fertilizer material as satisfactory as any other readily available form of nitrogen.

Early attempts to manufacture urea in this country were not particularly successful. During the war, as an emergency measure, du Pont manufactured a small quantity from calcium cyanamid. For a number of years, however, the urea used domestically has substantially all been of German origin. This held until the summer of 1932 when urea-ammonia liquor came on the market. The statistics of imports for urea are:

TABLE II

Year	Tons Per Year	
1926	189	
1927	407	
1928	894	
1929	2,294	
1930	9,196	
1931	7,131	
1932	3,829	
1933	(3,958)	9 months only

Urea has always been sold at a much higher price per unit of ammonia content than either ammonium sulfate or sodium nitrate and its use in agriculture has been thereby restricted, but it is seen that (except for the depression) urea has found a constantly increasing use in this country. Some of this imported urea was used for industrial purposes so it is not possible to say just how much went into agriculture.

III. *Research on Synthetic Urea:*

The fundamental reaction representing the synthesis of urea is $2NH_3 + CO_2 \rightleftarrows (NH_3)_2CO_2 \rightleftarrows (NH_2)_2CO + H_2O$. These reactions do not go to completion in either direction. Messrs. Krase, Gaddy and Hetherington, of the U. S. Department of Agriculture, have carried out extensive and valuable researches on the urea equilibrium. Their earlier work disclosed the relatively unfavorable conditions of urea synthesis as conventionally carried out; namely, with equiva-

lent amounts of ammonia and carbon dioxide and synthesis temperatures of about 140°C. In their experiments temperatures and pressures and proportions between reactants were varied to a considerable degree.

Du Pont's work in this field has been carried through under the guidance of Almquist, de Ropp, Hetherington and Miller. These men with full appreciation of the predictable mass action effects favoring urea conversion by increasing the temperature, pressure and proportion of ammonia in the reacting solution had as their goal the accomplishment of high percentage conversions with high rate of reaction from which fundamental data an efficient and economical continuous process could be developed.

The NH_3—CO_2—H_2O system at high temperatures and pressures is corrosive toward nearly every practical material of construction. As an example, some of our (own) early experiments were conducted in sealed gold tubes inside of an autoclave in which internal and external pressure on the gold tubing could be balanced. From this stage to a large successfully operating urea synthesis plant was a major engineering development.

Early in the experimental work on urea synthesis Dr. F. W. Parker of the Ammonia Department, from his background of study on the treatment of mixed fertilizers and superphosphate with anhydrous ammonia, realized that a solution of urea in liquid ammonia analogous to the equilibrium mixture made with excess ammonia might have advantageous properties in the ammoniation of superphosphate and mixed fertilizers. Objection had been frequently raised to the bad physical properties occasioned by the addition of urea to mixed fertilizers. Urea in a mixed fertilizer, except in the presence of proper conditioning agents, gives rise to an immediate pastyness or wetness and requires a long curing period before suitable physical condition can be obtained. The conditioning action of ammonia on superphosphate in the presence of urea, when the urea and ammonia are added in the form of a single solution, was found in actual practice to give quite surprising results. Mixed fertilizers treated with urea-ammonia liquor achieved at once a remarkably good physical condition. In many instances this has entirely eliminated the curing or storage period in the fertilizer factory. The quite fortuitous combination of being able to achieve a high efficiency in the synthesis of urea in the presence of excess ammonia and the marketing of this

solution substantially as it comes from the autoclaves has been probably the major advance in nitrogen fertilizer technology since the advent of the ammonia treatment of superphosphate.

IV. *Manufacturing and Marketing:*

A year and a half ago a full size unit to produce synthetic urea-ammonia liquor was installed at our Belle (Charleston, W. Va.) plant. Since then this material has been turned out regularly for delivery in tank car quantities. Naturally, some mechanical troubles were experienced at the outset, but the fact that they were few in number and were rapidly eliminated, speaks well for the thoroughness of the chemical engineering ground work and it is a further demonstration of the value of the testing out of a process by the intermediary operation of an adequate semi-works plant before attempting to start off on a large scale. The technical results obtained in the manufacture of the urea-ammonia liquor are a striking confirmation of the value of the theoretical mass action and equilibrium studies which preceded this design.

A diagrammatic flow sheet for the synthesis of the urea-ammonia liquor is as shown in Fig. 1. A photograph of one unit of the plant is shown in Fig. 2.

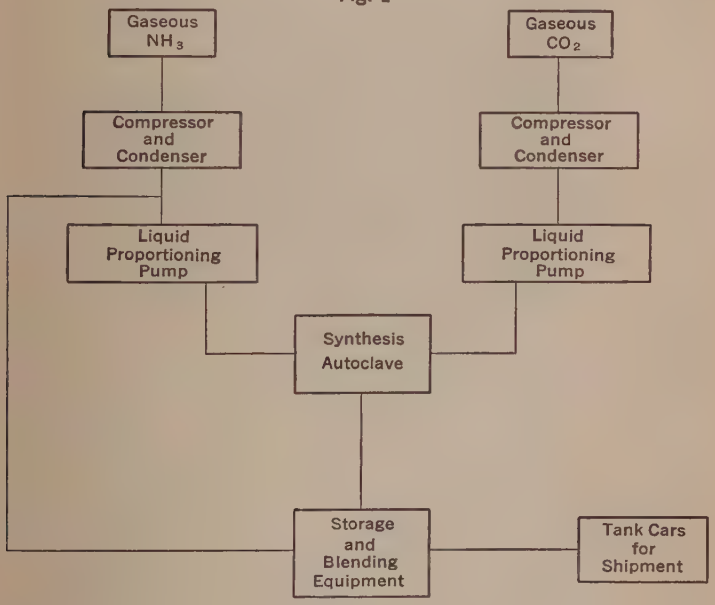
The properties of urea-ammonia liquor are well standardized. Its vapor pressure is about ¼ to ⅓ that of anhydrous ammonia under the same temperature conditions. The composition being marketed is as follows:

Urea	32.5%
Ammonia	28.9%
Ammonium Carbamate	18.1%
Water	20.5%
Total	100.0%

This liquor carries 55.2% of total ammonia or 45.5% nitrogen, of which two-thirds is in the form of free ammonia and one-third in the form of ammonia fixed as urea. The composition of the liquor is such that even under winter conditions there will be no danger of freezing or crystallization of the urea in transit or in storage. The liquor as marketed contains suitable inhibitors for the prevention of corrosion. It is handled throughout in standard steel tank cars and steel equipment.

The urea-ammonia liquor as received in a tank car at a commercial fertilizer plant is either stored in the regular anhydrous ammonia storage tanks with which many fertilizer plants are now equipped, or is diluted and pumped to the aqua ammonia storage tanks in such plants as are equipped to carry on ammoniation with aqua ammonia, or thirdly, in many cases it is used direct from tank cars. The method of use in the fertilizer mixing operation is the same as for ordinary anhydrous ammonia or aqua ammonia operations. Quan-

Fig. 1



tities to be used, etc., vary in different plants. One example for a 4-8-4 fertilizer may, however, be given. In this approximately 100 pounds of urea-ammonia liquor, which represents 2.75 units of ammonia, are used. This compares with a maximum of 100 pounds for aqua ammonia, representing 1.5 units of ammonia or 30 pounds of anhydrous ammonia, representing 1.5 units of ammonia. Speaking practically, excess ammonia beyond these quantities may cause undue reversion to tricalcium phosphate. The quantities of ammonia in the

above examples will not cause an increase in the citrate insoluble phosphoric acid of over 0.2—0.3%. It is thus seen from these examples that the use of urea-ammonia liquor permits the fertilizer manufacturer to introduce over one and one-half times as much nitrogen in solution form as can be accomplished with anhydrous ammonia for the same total amount of reversion.

Hitherto prices for imported urea in the United States have been from 60% to 100% higher than ammonium sulfate per unit of nitrogen content. At the present time, with imported urea quoted at $90.00 per ton or 8.0 cents per lb. of ammonia content and ammonium sulfate at $24.00 per ton or 4.8 cents per lb., the price differential is 66% higher for urea per unit of nitrogen content. Now, however, domestic urea-ammonia solution is priced down in the same range as ammonium sulfate so it can be seen that for the first time urea is available to the fertilizer industry at a non-premium price and in line with the very cheapest forms of nitrogen. This new mixture, therefore, is a distinct contribution to the farmer's need for cheaper, better nitrogen materials.

V. *Future Trends:*

(*a*) *General:*

It is believed the best program for the American nitrogen producers is to continue working closely associated with the organized mixed fertilizer manufacturers and distributors of this country. Cost reductions of the future in the manufacture of synthetic nitrogen products and in the manufacturing end of the mixed fertilizer business, as far as we can see, will be through technical refinements on one hand, and organization of manufacture on the other. The major economies to be effected will probably be achieved in the distribution end as relates to improvements in the credit and banking situation. The fertilizer manufacturer has been operating on a very close margin, no doubt even closer than the majority of other industrial enterprises. Those seeking to aid the farmer should appreciate this fully.

(*b*) *Technical:*

It is my belief that the chief advances to be expected in fertilizer technology will be in accomplishing increased suitability of our fertilizers to the soils on which they are used. The concept N-P-K as the sole criterion for a mixed fertilizer is no longer determinative

or sufficient. Other elements, sulfur, calcium, magnesium, manganese, etc., are well established necessities for certain soils and, not only are experimental stations studying these requirements, but also the forward looking fertilizer companies already are compounding their fertilizers to meet these conditions.

The next major advance in fertilizer utilization, to my mind, will be that relating to acidity control in the soil, and as a major factor influencing this, the control of potential acidities of mixed fertilizers and fertilizer salts will receive very detailed attention. For example, Tidmore [2] has shown in extensive field experiments the increased returns that may be secured from the control of the acidity factor in fertilizers.

The acidity of a soil is readily corrected by appropriate liming with either limestone or dolomite, and at the same time soil deficiencies of calcium or magnesium are remedied. Agricultural experiment stations have long advocated this practice, but it is a simple fact that the farmer has generally failed to follow this recommendation, and over the last years soils throughout the South and Southeast have become increasingly acid. The way to correct this situation is probably to manufacture properly compounded fertilizers, balanced as respects fertilizer composition and neutral or of low potential acidity so that no extra treatment or extra operation on the farmer's part will be necessary. If his soil is already very acid, it should be limed as a separate operation, but subsequent needs for lime would be met by the fertilizer.

Acidity of soils in the South and Southeast where heavy applications of mixed fertilizer have long been used has become an increasingly serious matter and fertility in many sections has been directly affected thereby. The major causes of acidity are depletion of the soil bases by the growing crops, the selective leaching of the basic constituents from the soil, and lastly, and probably the most important, the acidity occasioned by the application of acid forming fertilizer materials. All nitrogenous fertilizer materials now in the market with the exception of sodium nitrate, calcium nitrate and cyanamid are acid forming to a greater or less degree. Any form of organic or ammonia nitrogen applied to the soil is converted ultimately to the nitrate form by nitrification, and except as adequate basic constituents are simultaneously provided, there must be production of acidity equivalent to the nitrogen added. Of all fertilizer

salts in current use, ammonium sulfate has the least favorable rating as respects acidity. For each molecule of ammonium sulfate added to the soil and nitrified there must be liberated, in addition to the two molecules of nitric acid formed on nitrification, also one molecule of sulfuric acid from the SO_4 set free by the nitrification of the ammonium base. The sulfuric and nitric acids demand corresponding amounts of base from the minerals in the soil and the reserve

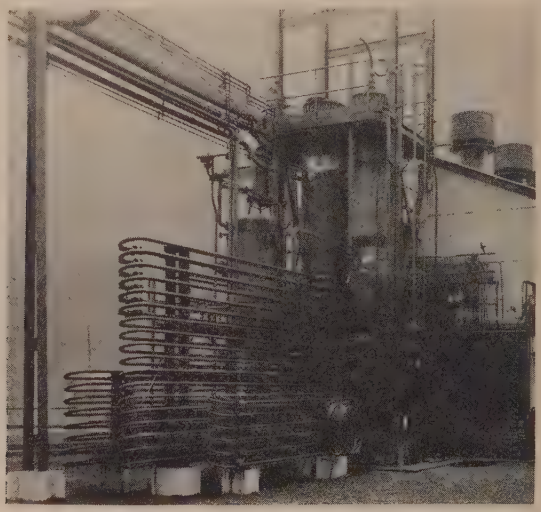


FIG. 2.—One unit of the Urea Plant.

stock of basic material in the soil is thereby depleted. The explanation of the production of acidity by fertilizer ingredients applied to the soil has been most clearly set forth by Pierre.[3] Long time field tests confirm the theoretical viewpoint and practice has established that 1.2 pounds of calcium carbonate are required per pound of ammonium sulfate applied if the soil reaction is not ultimately to be effected adversely.

The principal nitrogen carrying fertilizer salts actually rate as follows as respects acidity production. This acidity is expressed as the pounds of calcium carbonate required to neutralize the acidity produced per unit of nitrogen content in the respective fertilizer material.

TABLE III

Material	Per Cent Nitrogen	Equivalent Acidity Lbs. $CaCO_3$ Required Per Unit (20 lbs.) Nitrogen Content of Fertilizer Salt
Cyanamid	22.0	(Basic and corrective to acidity)
Sodium nitrate	16.4	(Basic and corrective to acidity)
Calcium nitrate	15.0	(Basic and corrective to acidity)
Calnitro	20.5	0
Organic nitrogen fertilizers	...	15 *
Anhydrous ammonia (or aqua ammonia)	82.4	36
Urea	46.6	36
Ammonium nitrate	35.0	36
Ammonium phosphate	11.0	107
Ammonium sulfate	21.1	107

* Variable from 36 pounds to basic.

It is evident that in general the nitrogen compounds principally used for top dressings are basic in reaction, whereas the forms of nitrogen conventionally used in mixed fertilizers are acidic. There is a wide interest now awakening in this subject of acidity and indications are that not only the state and government experiment stations, but also the control officials and the fertilizer companies themselves, are taking cognizance of it. Pierre has recently carried his acidity work further to include an analytical method for determination of the net ultimate acidity of any mixture of fertilizer materials.[4] With this tool in hand, it seems reasonable to expect that it is only a question of time when this acidity situation will be taken care of through proper correction of formulation.

Mehring and Peterson's recent survey[5] of trends in fertilizer formulation over the last 30 years brings out among other things three important and striking facts. These are:

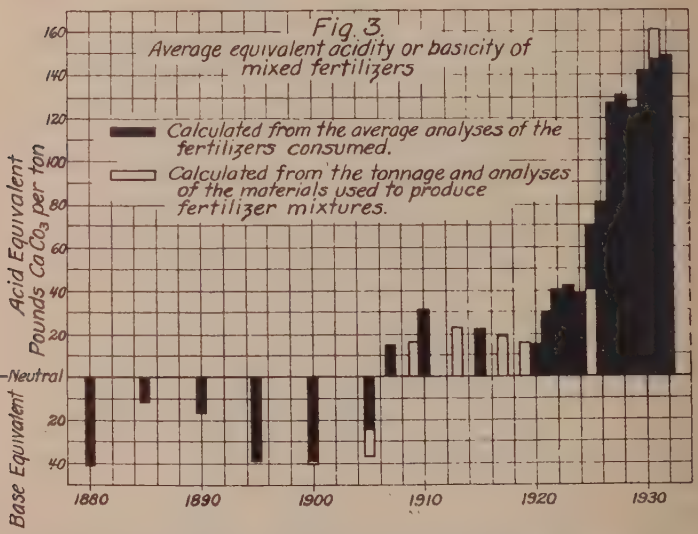
1. The P_2O_5 content of complete fertilizers has remained fairly constant since 1890, an average figure being about 9.4%. The nitrogen and the potash content, on the other hand, have increased 50 per cent and 100% respectively during the same period with most of the increase coming during the last 8 years. The complete fertilizer of today will average closely to a 3.5% nitrogen, 9.6% P_2O_5, 5.2% K_2O mixture.

2. Their data on the sources of nitrogen used in mixed fertilizers confirms that the equivalent acidity of fertilizers has increased rapidly in recent years. Ammonia and its salts constituted 2.1% of the nitrogen in mixed fertilizers in 1900, 23.8% in 1919 and 61.2% in 1921. In the same years 91.0%, 53.6% and

18.8% of the nitrogen was derived from natural organics; and 6.9%, 19.7% and 11.6% from nitrate of soda.

In Fig. 3 is shown graphically values calculated by Mehring and Peterson [6] for the acidity (in limestone equivalents) for the average mixed fertilizer marketed in the United States from 1880 to the present time.

3. The filler content of fertilizers has increased from 6.8% in 1900 to 12.3% in 1925 and to 15.2% in 1931. This increase in filler took place despite the fact the average total plant food content increased from 14.1% in 1900 to 17.9% in 1931.



Calculation by Pierre's method of the equivalent acidity of the present day average grade of mixed fertilizer indicates that it requires 200 lbs. of calcium carbonate per ton, or 10.0% to render it neutral in actual soil reaction. Mehring and Peterson's data just given with respect to percentage of inert filler now employed show there is ample margin in present fertilizer formulation to permit substitution of adequate limestone or dolomite for this acidity correction. MacIntire and his associates [7] have shown that limestone vs. dolomite can be used without loss of ammonia or reversion of P_2O_5.

Another factor that is receiving increasingly careful scrutiny is the question of the relative efficiency and advantage of so-called

"organic" nitrogen carriers versus "inorganic" nitrogen fertilizer materials. Urea has conventionally in most localities been classed as an "organic" form although some groups now advocate a classification on a "water soluble" and a "water insoluble" basis. This reclassification would place urea in the "water soluble" nitrogen category, and such other fertilizer materials of animal or vegetable origin as cottonseed meal, tankage, dried blood, fish scrap, etc., in the "insoluble nitrogen" category.

Organic forms of nitrogen have found wide popularity and acceptance in the past, and since many of these materials have had alternative outlets for stock feeding purposes, much higher prices have been paid for them for fertilizer purposes than for the corresponding inorganic nitrogen carriers. My understanding is that careful unprejudiced analysis of available modern agronomic data does not indicate these materials to merit a premium classification, and in fact in many cases there is actual evidence that the water insoluble forms of nitrogen are less efficient over all than the water soluble forms.

Likewise, there is often a misunderstanding of the significance of the term "water solubility" and the supposed consequent liability of chemical forms of nitrogen to be leached from the soil. Nitrate salts leach readily and quickly from sandy soils during a wet season, whereas ammonia salts and derivatives, such as urea, are held so strongly absorbed or fixed by the humus and clay constituents in the soil that they are substantially unleachable and only as bacterial action accomplishes nitrification and oxidation of the ammonia to the nitrate form is there any tendency toward leaching or washing away.

Recently wide interest has attached to work by Byers on the one hand and Davis on the other, both of the Department of Agriculture in Washington, on the subject of ammoniated peat as a fertilizer material. Apparently a considerable part of the ammonia which can be combined with peat under high temperature autoclaving conditions passes into chemical combination of the truly organic "water insoluble" category. The careful work now under way in numerous quarters to evaluate the fertilizing value of this ammoniated peat material will afford pertinent evidence on the general merit of organic water insoluble forms of nitrogen as fertilizer materials.

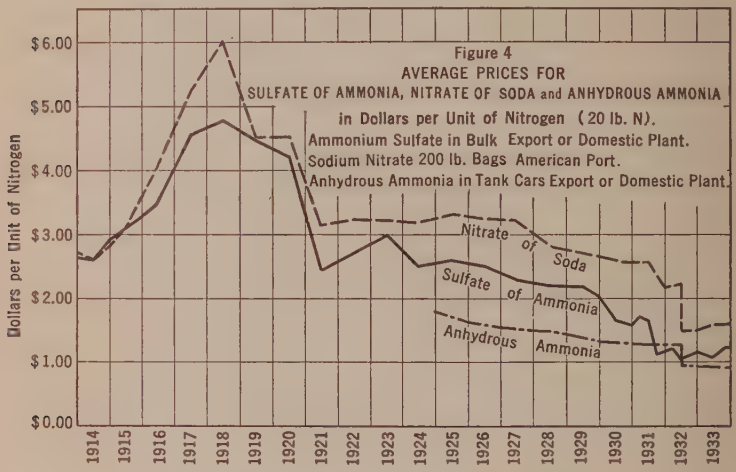
VI. *Other Aspects:*

The preceding discussion of these problems that face nitrogen

manufacturers and users discloses what we conceive to be the approaching advancements in the industry. In concluding, some further general aspects and trends are worthy of mention.

Prices of inorganic and synthetic nitrogen carriers are down very nearly to bed rock. The course of these prices since 1900 is shown in Fig. 4.

Ammonium sulfate now sells around $24.00 on port delivery basis. With proper allowances for manufacturing and distributing expense often no net credit whatever is obtained for the ammonia content of



the material. Some factors favorably situated in the industry may perhaps net as much as 1.0c or at the most 1.5c per pound of ammonia content.

The Chilean nitrate industry, in spite of great technical improvements, has been forced to undergo a drastic financial reorganization. Capital charges are apparently to be so scaled down that the Chilean industry will be able to set up a sales price structure which will represent out-of-pocket costs of production, delivery and sales, plus relatively very small fixed charges and very moderate tax returns to the Chilean government.

In these past years of drastic price declines the synthetic nitrogen industry also has shown no possibilities for even meagre earnings, and it is only through the accomplishment of technical betterments and refinements and through steadily increased outputs that the syn-

thetic industry has been able to hold its ground. Today I believe it can be said that no important reductions in operating or manufacturing expenses are to be expected for any of the principal nitrogen fertilizers. Further reductions in price may come through better organization and control in the distribution and banking and credit branches of the fertilizer industry, but again it is my belief that the major prospects for progress in the future will come from an increased efficiency in the use of the fertilizers themselves and a better knowledge of how to apply the fertilizers in the field.

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Discussion

Chairman Dorr: I am sure we all appreciate this most valuable paper. In view of the lateness of the hour it will be necessary to postpone discussion until our next session as we have scheduled now a paper on "The Development of Air Conditioning in Industrial, Residential and Public Buildings" by Mr. P. L. Davidson of the Carrier Engineering Company which has been the pioneer in this industry. Mr. Davidson.

THE DEVELOPMENT OF AIR CONDITIONING IN INDUSTRIAL, RESIDENTIAL AND PUBLIC BUILDINGS; ITS EFFECT ON HUMAN BEINGS; THE FACTORS WHICH ENTER INTO ITS DESIGN

By P. L. DAVIDSON *

Air conditioning was born in Industry. It was the cotton spinner and weaver, the printer and the confectioner who first recognized the necessity of controlling the temperature and humidity of the air in which their products were processed. They recognized the fact that the control of the conditions of the air was economically essential if they were to adapt their factories to modern mass production. Their primary object in its use was for its direct effect on the product itself, and they gave only secondary consideration to its indirect effect of the increase in human efficiency resulting from the maintenance of more comfortable working conditions.

In certain industries, the relative humidity best suited to the processing of the product may not be within the human comfort zone; but in most such cases, if the temperature is also controlled, optimum conditions both for the worker and the product can be maintained.

Even in those industries which manufacture products not affected by variations in either temperature or humidity, the beneficial effect of maintaining the air conditions within the comfort zone solely for its effect on the efficiency of the workers has been found to be economically desirable. The recognition of this fact has enormously widened the field of the air conditioning industry. Comfort is one of the fundamental basic sensations for which Man has always striven and fought to enjoy. Consequently, any industry such as air conditioning, which can fulfill this desire and at the same time meet an economic need, will readily get the public recognition that it deserves. The recognition of this particular virtue is undoubtedly responsible for the very large growth in the last few years of the air conditioning industry, which is twenty-five years old.

It is therefore quite fitting that any study of air conditioning should include not only a study of its effect upon the processing of

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materials, but also its effect on human comfort and efficiency; and probably more emphasis should be placed upon the latter as that has a universal application, while the former is limited to those products which are affected by variations in temperature and humidity.

Before we consider these questions, it is appropriate that we relate the history of the science of air conditioning.

History

Long is the history of Man's attempt to build dwelling structures and to control the temperature therein. The early stages of the process by which true architecture grew out of the first rude attempts at building are impossible to trace. The oldest existing monuments of Chaldea and Egypt belong to an advanced civilization. But we can study the development of architecture from the Megolithic remains of Europe and Asia through the Greek, Romanesque, Gothic, Renaissance and other styles up to such structures as the modern functional air conditioned factories, homes and office buildings of the day.

In the same way, we can follow Man's attempt to condition air. From prehistoric times, he has striven to control some of the factors which constitute air conditioning but, until recent years, he has only been successful in the partial control of the first factor—temperature. With the discovery of fire, Man controlled to some degree the temperature in his cave, wigwam or house; and this discovery enabled him to extend his domain from the semi-tropical regions adjacent to his birthplace between the Tigris and Euphrates Rivers north and south to the proximity of the Poles. Living conditions in prehistoric times imposed hardships which would be found intolerable and perhaps unendurable by our generation.

Until the past few years, the methods of utilizing fire to obtain comfort were, for the most part, little different from the open fire of prehistoric man. The man who discovered fire would find an English fireplace but a slight improvement over the open fire in his own crude shelter. Man then developed the Franklin stove, which paved the way for the design of other stoves which more effectively utilized and distributed the heat produced by fire. Next came the warm air furnace, which made it possible to warm an entire building from a central source. Then came hot water as a carrier of heat, followed by the steam and vapor systems which have been developed to a very high degree. But, just as architects met changing conditions by turning

from the old forms to the skeleton-like skyscrapers of today, so have our heating systems been developed to meet new architectural demands—until one finds in the modern building a union of the most modern functional architectural design with an equally modern air conditioning system. (Fig. 6.)*

It was left for the engineers of this generation to pioneer the research into the various factors which constitute true air conditioning. They discovered the laws [2] pertaining to it and so developed the technique of their application that air conditioning can now be applied economically and efficiently to any structure that the architect may conceive.

As human culture increases, so do our research problems. Modern concert halls will be designed and built, and the air conditioning systems serving these halls will control not only the factors which determine human comfort and efficiency, but also seek to enhance human aesthetic enjoyment of music and its allied arts by controlling the effects of temperature and humidity on the production and transmission of sound. On this subject,[29,30,51] Vern O. Knudson has conducted some brilliant research and has shown us the effect of temperature and humidity on the absorption, reflection and reverberation of sound. He states that proper control of humidity, as well as temperature is necessary in order to insure the highest acoustical quality in all auditoriums as the reverberations of the high frequency components of speech and music is affected more by the condition of the air than it is by the nature of the boundary walls.

Air conditioning has made great progress, but the surface of this new industry has scarcely been scratched. Why should there be such a need for air conditioning? Did not our forefathers prosper without it? It is a very appropriate question. Let us analyze it. Our forefathers lived what we would call today a very rural, or at least a suburban existence. What towns there were, were comparatively small. There was no great concentration of light and power, with their necessary corollaries—heat, noise and dirt. Our forefathers baked their own bread, tanned their own leather, raised their own food, spun and wove their own cloth. If conditions were not right for weaving, they either waited until the weather changed or moved their looms to the cellar, which was comparatively humid.

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* All figures illustrating this paper appear as an Appendix. See page 88.—EDITOR.

Then came the Industrial Revolution! John Kay invented the fly shuttle; James Hargreaves, the spinning jenny; and Richard Arkwright, spinning frames driven by water power. The machinery Arkwright developed was so bulky and heavy that it was impossible to install it in the ordinary buildings of the day. Special buildings were developed to house it, and these were called factories. Arkwright was truly "the father of the factory." With the perfection of his machine and the development of Samuel Crompton's spinning mule, Edmund Cartwright's power loom, Eli Whitney's cotton gin and James Watt's steam engine, these factories grew larger and larger, increased in number and concentrated in the sections of the country where cheap water power, transportation and labor were available. From these, our enormous manufacturing cities grew. The individual no longer wove his own cloth. He labored in another industry, for which he received the means which enabled him to buy the cloth woven by others in other factories. With developments such as these, money and our complicated monetary system arose to replace trade by barter.

With the concentration of machines in factories, the heat produced by the power that drove them increased the temperature and lowered the humidity to a point far below the natural humidity outside. Sound economics dictated that these machines should not be shut down just because of low humidity or high temperature, and methods of artificially raising the humidity and lowering the temperature were developed. This, as applied in the cotton industry, was undoubtedly the first example of Man's attempt to control humidity—one of the three essential factors of air conditioning.

Today, there are some two hundred different industries which require partial or complete conditioning of the air for some or all of their manufacturing processes. The most important of these is the manufacture of cotton, silk and rayon textile yarns and fabrics.

Cotton, Silk and Worsted

It is necessary to maintain constant humidity conditions in the processing of cotton, starting with the picker room, on through carding, drawing, roving, combing, warping, winding, spooling, twisting, spinning (Fig. 1) and, finally, weaving (Fig. 2). The relative humidities necessary for these different processes range from 50% to 95%.

In the silk, wool and worsted industries, the control of humidity is also essential in practically all of the operations. Before the silk yarn is knitted into hosiery or underwear, the yarn should be conditioned to remove the kinks or set the twist, and the knitting operation should be carried out in a humidified room. The control of temperature is also essential to the manufacturing operation in the knitting of silk hosiery.

Rayon

The rayon industry in this country had its birth at a time when air conditioning was becoming an established art. It therefore grew up with the aid of air conditioning and did not adopt it, as silk and cotton did, only after the complications of its size made it essential. As a matter of fact, without the control of temperature and humidity, it would have been impossible for the rayon industry to have grown at all.

In the viscose process of manufacturing rayon, air conditioning is essential throughout the entire complicated process. It is used in the storage room where the raw product, cellulose in the form of wood pulp or cotton linters, is stored before using. It is essential in the soda room, where the wood pulp is treated with caustic soda in presses and pfleiderers; also, in the storage, where the cellulose in the form of "crumbs" from the pfleiderers is stored before it proceeds to the churn room, where proper ventilation is required during the process of treating the "crumbs" with carbon bisulphide. After mixing and filtering, the green viscose goes to the viscose cellars, where a slow chemical reaction termed "aging" takes place. As the manufacturing schedule allots a certain definite time to this reaction, the temperature must always be kept constant to insure that this chemical reaction proceeds at a constant rate.

In the next process, where the liquid viscose is spun (Fig. 3) into thread, air conditioning is essential—first, to retard evaporation and thus prevent crystalization of the sulphates on the finished thread; and, second, to provide adequate ventilation, both supply and exhaust, to dilute the fumes from the sulfuric acid bath and exhaust them from the room.

In the reeling, sorting (Fig. 4), inspection, spooling, quilling and warping rooms, air conditioning is again used; and, particularly, in the sorting and inspection rooms, where it has proven desirable to maintain comfortable temperature conditions to improve the efficiency

of the workers at the monotonous and arduous task of inspecting the finished silk, and to prevent the soiling of the skeins with the perspiration of sweaty fingers. The relative humidity is held constant to maintain the hygroscopic rayon at the correct moisture content or regain.

In the further operations of knitting or weaving, air conditioning again plays an important part.

Cigarettes

The air conditioning system is one of the necessities of the modern cigarette factory, starting with the sweat house, where the tobacco in hogsheads is kept at a high relative humidity under temperatures of 90 to 100 deg., to control the fermentation which ages the tobacco and greatly improves its quality. Next, in the "ordering" or softening operation where the tobacco on belts is passed through a softening machine, an air conditioning system automatically heats, moistens and cools the tobacco for stripping, makes the stem of the leaf soft and pliable, the leaf itself slightly drier and crisp, and maintains a constant humidity to hold the leaf in its proper condition.

From the stripping room, the tobacco goes to the casing department, where it is blended and sprayed with the seasoning juices; then to the drier, and next to the bulk room, where the tobacco is stored to insure the even distribution of the flavoring juices in the tobacco. This room is of course conditioned to insure controlled and proper seasoning without change in the order of the tobacco.

From here, the tobacco goes to the cutting room, where it is cut into shreds ready for the cigarette. This room must be carefully conditioned to keep the strips soft and pliable so that the machine will cut, and not break or tear the tobacco.

After the cutting operation, the tobacco is dried in a rotary cylinder and is then placed in cut storage, where it remains twenty-four hours or longer, in order to permit the seasoning juices to become evenly distributed throughout the cut mass. Cutting "bleeds" the tobacco and the storage period allows the tobacco juices to unite with the flavoring juices. This room must be properly conditioned to keep the tobacco in the right state for the making operation.

In the making room, automatic machines form the cigarette with remarkable precision and rapidity. This room must be accurately conditioned. If the tobacco is too moist when the cigarette is being

made, it will pack and form a hard cigarette which will not smoke well. If too dry, the tobacco will fall out of the paper tube and the cigarette will be flimsy and unsatisfactory. Also, if the condition of the tobacco varies due to changes in the atmosphere, the making machines must be readjusted to meet the new conditions. The maintenance of constant temperature and humidity will keep every machine in constant operation at maximum capacity.

The packing department should also be air conditioned, to keep the tobacco from drying and to insure a fresh cigarette in every package.

Cigars

In the cigar industry, air conditioning also plays its part. It is necessary for two reasons—one physical, the other chemical. Tobacco cannot be handled until it is rendered moist enough to be soft and pliable, and it must not be too moist lest it mould and spoil or lose its fine flavor and aroma.

Before the development of air conditioning, the only method of moistening the tobacco was by spraying or dipping it in water. This was an uncertain and dangerous process and often caused deterioration in the quality of the tobacco or "darkening," a loss of color which seriously affected the value of the cigar.

In the modern cigar factory, air conditioning brings the filler tobacco to the condition which is best for stripping, or the removal of the stem from the center of the leaf. This operation requires considerable moisture so that the leaves will be very pliable and permit the removal of the stem without tearing or loss of the desirable part of the leaf itself.

Next, the filler must be deprived of a part of its moisture and put into suitable condition for rolling. This is usually spoken of as drying, but it is more aptly termed "conditioning" since the leaf must retain a definite moisture content.

The wrapper tobacco must be conditioned and handled separately. It is more delicate and its color must be preserved with jealous care. The wrapper leaves must be stripped and booked—that is, arranged with the leaves in regular order ready for the quick fingers of the roller girl or the rolling machine operator. In all these processes, the temperature and humidity must be controlled, else loss or deterioration will inevitably occur.

In the rolling rooms, the air must be in proper condition to keep the tobacco pliable, yet strong and resilient; and this is true whether the rolling be done by hand (Fig. 5) or machine. Air conditioning is required also in the sorting and the cellophaning and banding rooms.

The cigar makers who roll cigars by hand require careful training over a period of months, and when so trained they become valuable, expert employees. In the past, the health record of the cigar roller was not enviable. Today, air conditioning has made cigar rolling a clean, healthful and well-paid occupation from the worker's standpoint; and for the manufacturer, it has minimized absenteeism and insured maximum production as an every day routine.

Of course cigars, to insure their fine smoking qualities, must be kept in conditioned air until they are smoked.

Air conditioning has made possible the transfer of some of the operations in the manufacture of cigars from Cuba, where the natural temperature and humidity is better suited for the hand rolling of fine cigars than the climate of the northern part of the United States. Labor conditions in Havana made it desirable to manufacture the famous Corona cigars in Trenton, New Jersey. Without the science of air conditioning, it would have been impossible to do this, but today the famous brand of Corona cigars is being manufactured in an air conditioned factory in Trenton.

Air conditioning plays an important part in the weekly production of 8,000,000 Bayuk Philadelphia cigars, the world's largest selling cigar at any price, and helps to cut production costs so that in spite of the recent increases in taxes, labor and tobacco, this cigar still sells for five cents. Congress' Blackstone and Consolidated's Forty-four and Harvester are some of the other brands manufactured in air conditioned factories.

Other Industries

In the candy industry, the control of temperature and humidity is essential in the manufacture of chocolate candies. It is also required in the hard candy industry to give these candies the fine sheen which makes them attractive to prospective buyers, and to keep them from sticking together.

During the recent war, it was considered essential to try all possible methods of manufacturing nitrates. One method was by fractional crystallization, but the chemical reaction demanded that the solution be

kept at a constant temperature with practically no variation to obtain the maximum or practical yield. Considering the size of the operation and other complications, this seemed almost an impossible task, but the correct application of air conditioning made this a practical possibility. This method was used successfully during the war. However, it was not the cheapest method of producing nitrates, and has since been abandoned for more efficient methods.

In the printing industry, air conditioning is necessary to keep the hygroscopic paper at the correct moisture content to insure quality printing; and in multi-color work and lithographing, it is necessary to keep the large sheets of paper from changing dimensions due to variations in the humidity and thus coming out of register.

The manufacture of asbestos, the ceramic industry, the production of capsules, the manufacture of cellophane, chewing gum and photographic film, the baking of bread, the brewing of beer, the ripening and storage of bananas, the manufacture of such breakfast foods as postum, the packing of coffee, the milling of flour, the manufacture of sausage, the growing of mushrooms, the manufacture of matches, the packing of effervescent salts and the manufacture of rope are a few of the industries which have found air conditioning an essential aid.

Effect on Health, Comfort and Efficiency

Our industrialists are well aware of the value of air conditioning for its effects on the products they manufacture. They are just beginning to realize that air conditioning installed only because of its beneficial effects on human comfort and efficiency is a valuable tool which will pay a handsome dividend. In Fitchburg, Massachusetts, a factory built without windows, manufacturing a product which in itself is not affected by the condition of the air, is completely air conditioned. Windowless, the illumination in the factory will always be constant regardless of the fluctuating light outside, and the air conditioning and constant illumination will increase the efficiency of the workers and standardize the uniformity and quality of the product manufactured, and thus reflect increased profits.

Just as the concentration of mill machinery necessitated the humidification of the factories processing hygroscopic materials, the modern concentration of buildings and people in our cities has so contaminated the atmosphere in which we live that it is essential to our health and well-being that city air be conditioned. The weight of

the food eaten daily by the average person is 3½ lbs., the weight of air breathed is 35 lbs. The fact that 40% of our energy is derived from food and 60% from the air we breathe shows the relative importance of conditioning the air we live in. In spite of our smoke laws and in spite of our advanced knowledge of combustion, our chimneys and incinerators spew forth cinders, soot and sulphur dioxide; our automobiles pollute the air with carbon monoxide [15] and oil fumes; the dirt and debris of years collects and remains in our streets, in spite of the efforts of our Street Cleaning Departments. Our buildings (Fig. 6) rise higher and higher, built on practically every available plot of land. The obsolete are torn down, only to make way for a greater concentration of parked automobiles. The light is shut out and the natural air circulation impaired. The rays of the sun which do reach us are filtered through the smoke and dirt constantly suspended in the air above us. This acts as a screen which prevents a great proportion of the beneficial actinic rays of the sun from reaching us.

We talk of "fresh" air. In the strict sense of the word, there is no such thing as fresh air. The air we breathe daily is the same air here billions of years ago—the same air our ancestors breathed over and over again. If by "fresh" air we mean oxygen and nitrogen, uncontaminated by dirt, bacteria or toxic gases, we will find that even this is not to be found within our modern cities.

If we are to control air conditions for human comfort and efficiency, we must study the effect of such conditions on the human mechanism; and also study that mechanism to determine just how it operates, where and how the bodily heat is produced and how, and how quickly, that heat is or should be dissipated.

Extensive research investigations conducted jointly by the United States Public Health Service, the United States Bureau of Mines and the Research Laboratory of the American Society of Heating and Ventilating Engineers have determined the effect of atmospheric conditions on the human body. They have correlated the physiologic responses of the body to a wide variety of environmental temperature conditions, and have determined the temperature, humidity and air motion combinations which give equal sensations of warmth or cold. The index of these sensibly equivalent temperature and humidity combinations has been termed "effective temperature." [3] A scale indicating the various combinations of the physical air factors which are

essentially equivalent has been developed as a result of these studies.[5,6,7,18]

It was found that the combinations of the physical properties of the air lying along the line indicated as 66 deg. effective temperature between the limits of 70% and 30% relative humidity, gave the most desirable sense of comfort to the large majority of individuals used as subjects in the experiments, and this line is called "the comfort line" of the scale. At effective temperatures above 70% and below 30% relative humidity, the air actually has the same capacity to absorb heat from the human body, but beyond these limits certain physiological reactions occur which prevent effective temperatures beyond the limits of these relative humidities from being included in the true comfort line or zone.[22]

Later experiments conducted by the Harvard School of Public Health established a comfort zone (Fig. 7) and showed that, during the summer season, the comfort zone slides up the scale, with 66 deg. and 75 deg. as the lower and upper limits, and 71 deg. as the maximum comfort line; and that during the winter season, the comfort zone shifts downward, ranging from 63 deg. to 71 deg. effective temperature, with a maximum comfort line of 66 deg. Experience has also demonstrated that the inside temperature should bear some relation to the temperature outside, that higher inside effective temperatures should be maintained with higher effective temperatures outside. In terms of dry bulb temperature, this means that a temperature not lower than 80 deg. should be maintained inside when the outside temperature is 95 deg. or more; when it is 90 deg., 78 deg.; when it is 85 deg., 77 deg.; when it is 80 deg., 75 deg.; when it is 75 deg., 73 deg.; and when it is 70 deg. outside, 72 deg. These differentials should of course be modified slightly in accordance with local conditions, taking into consideration the average fluctuation of the outside temperature and the customary clothing worn by the people of the locality. This temperature differential should be varied in England, where the customary clothing in summer is heavy tweeds and waistcoats and where the outside summer temperatures are comparatively low. Philadelphia, New Orleans, Atlanta and San Francisco would all require different modifications to compensate for their different outside temperature [20] conditions and the clothing of the people of these localities. A theatre, restaurant, department store and office building would all require different variations from this schedule. In a climate such as

that of Philadelphia, where the summer temperature may range from 70 deg. to 95 deg. within one week, it would never be desirable to carry the room temperatures as low as 72 deg. to take care of a cool morning or a cool day during mid-summer. In climates such as that of Philadelphia, interior summer dry bulb temperatures ranging between 75 deg. and 80 deg., with a relative humidity of 50% or below, have proven very satisfactory for office buildings. Lower temperatures should of course be maintained during the fall and spring, when people have become accustomed to cool weather outside and are wearing heavier clothing. Under these circumstances they have become acclimated—that is, their basal metabolism has adjusted itself to the lower outside temperature conditions.[19,8]

Cooling in summer is probably the most spectacular development of air conditioning. But air conditioning is of vital importance in winter; in fact, of the two, it is probably the more important. We certainly spend more of our time indoors in winter than in summer and, in many localities, the heating season is a good deal longer than the cooling season. All the available evidence on this subject indicates the desirability of providing a fair percentage of moisture in the air; that air low in moisture content tends to dry up the mucous membranes of the nose, throat and lungs, thus lowering the resistance of these organs to infection. Dry air also irritates the sensitive nerve endings of the skin and produces nervous reactions which are, to say the least, undesirable.

Dry air indirectly affects our health and comfort [12] by drying the furniture, oil paintings, woodwork, draperies and rugs and carpets, shortening their life by lowering their resistance to abrasion, and thus liberating an excessive amount of dust and bacteria which increases the liability of infection.

The incidence of sinusitis [11] is attributed to the vasomotor effects of sudden chilling of the mucous membranes which have been subjected to dry, overheated indoor air. Persons with sinus trouble in our cold northern climates are often advised by physicians to go south where the climate seems to be more favorable to the course of sinusitis. The warmer southern climate, the higher humidity and the smaller temperature variability are probably responsible for the beneficial effects. This general view is fairly well in accord with Huntington's statistical data.[1]

The use of air conditioning [53] in relieving the symptoms of hay

fever and asthma due to substances inhaled was first noted by Dr. S. S. Leopold and C. S. Leopold in 1925. (Later experiments made at Johns Hopkins Hospital [21] confirmed their findings.) Numerous investigations are now being made in the conditioned Philadelphia Saving Fund Building by Dr. J. Alexander Clark, Jr. Experiments to date indicate that the benefit is secured by the cleansing action of the conditioning apparatus in removing air-carried foreign substances which cause the symptoms. Relief lasts only as long as the patient is in the conditioned space.

Results on asthmas of the bacterial type are generally negative and little is known of the effect of temperature and humidity on these and allied allergic disorders.

It has been demonstrated, also, that higher temperatures are required for comfort when the percentage of moisture is low. Excessively high humidities, on the other hand, are undesirable because of their interference with the normal evaporation of moisture from the skin. Excessive frosting or condensation on windows and walls likewise discourages the use of high humidities.

The average winter temperature in the vicinity of New York and Philadelphia is 31 deg., with a relative humidity of 70%. When this outside air is raised to a temperature of 70 deg., the relative humidity drops to 18%.

Under such conditions, to raise the relative humidity of indoor air necessitates adding large amounts of moisture. The average house, even when weatherstripped and thoroughly insulated, will require the evaporation of eight gallons of water per day to properly humidify the air. Many of us have experimented with the placing of pans of water on our radiators in order to supply a sufficiency of moisture. When you realize it takes approximately eight gallons of water a day, you can readily see that such a make-shift system gives inadequate evaporation and does very little good.

Simple humidifier units (Fig. 8) which can be installed in an existing home (Fig. 9) for a moderate cost have been developed. The best of these consists of a fan, heater and spray of the target type which practically eliminates the troublesome clogging of sprays. This unit can be installed in the basement, generally under the hall, and delivers humidified air to the house through a grille in the floor.

Statistics show that the death rate from influenza,[14,12,13] bronchitis and pneumonia reaches its peak in the winter, but it is largely indoor

weather which is responsible. An actual survey in some industrial plants during the winter of 1929-30 showed that 40% of the absenteeism was caused by the common cold. The economists who have studied the results of this survey and other significant data tell us that the common cold costs the American people ten billion dollars a year.

Ellsworth Huntington has done some brilliant work along these lines and in his book "World Power and Evolution," he points out that in the dry interior of the United States a relative humidity of less than 30% increases the death rate by at least 10% above that which prevails when the relative humidity is 70% or higher.

Experiments [22] have been made on human subjects exposed to abnormal temperatures and humidities under accurately controlled environmental conditions. It was found that man loses his physiological efficiency beyond certain temperature limits. For a man at rest and in still air the upper limit lies around 90 deg., saturated or 90 deg. effective temperature. The cooling effect of a velocity of 200 feet per minute shifts the upper limit to 95 deg. An air velocity of 400 feet per minute raises the limit still higher. When physical work is being done, the limit of heat which can be tolerated physiologically drops considerably below 90 deg. effective temperature. When muscular work at the rate of 90,000 foot pounds an hour is being performed, the limit is about 80 deg. effective temperature. Seasonal variations and differences in clothing will modify these results slightly.

Above these temperatures,[16] the mechanism of the body is affected by overheating. The body makes strenuous efforts to resist the rise in its temperature by the evaporation of perspiration, but above these temperatures the limit of action of this natural thermostatic control is reached, and altered physiological reactions occur.

The more obvious of these takes place in the circulatory system, apparently starting with the rise in skin temperature. The heart rate increases. Flushing of the skin and profuse sweating ensue. As sweating continues, the volume of the circulatory blood supply may be materially reduced, through loss of water from the blood. The result is insufficient blood returning through the veins, for which the heart compensates by beating faster. In a very hot atmosphere, the systolic blood pressure rises and the diastolic pressure becomes immeasurably small. The fall in diastolic pressure is probably caused by the failure of the surface blood vessels of the skin to maintain their tension. Simultaneously with these circulation changes, the temperature of the body rises.

The extent of the discomfort experienced appears to be better determined by the increase in pulse rate than by the rise in body temperature. This does not mean that the fast heart beat is the cause of the discomfort, but it is the measure of it.

When the pulse rate exceeded 135 beats a minute, the subjects of these experiments complained of discomfort, became restless and irritable, complained of headache, palpitation of the heart and extreme thirst. After the pulse rate exceeded 160 beats a minute, the condition became distressing and unbearable; dizziness and confusion resulted, followed frequently by nausea and numbness or soreness of the face. As the severity of the test increased, a feeling of "floating in the air" came on, and experiments were discontinued for fear of heat stroke. When the subjects left the test chamber, although their internal temperature increased slightly, the pulse rate began to drop rapidly and their condition immediately improved and returned to normal within a short time.

The exhaustion and weakness following the subjection of human beings to very high temperatures and humidities over a short period is not as severe as when subjected to moderately high temperatures and humidities over longer periods.[17]

These few illustrations of the many changes occurring within the human body under conditions which prevent the usual loss of surplus body heat signify the necessity for controlling unfavorable temperature conditions wherever human beings must live. These disturbances of the body functions, even when slight, exert a marked effect on human efficiency. According to these researches, the maximum amount of work was performed between the effective temperature limits of 40 deg. and 75 deg. Subjects of the experiments were capable of performing four times more work in a temperature of 100 deg. with a relative humidity of 30% than they could in a saturated condition of 100 deg. With the ordinary summer humidity of 60%, the subjects performed about five times more work in a temperature of 90 deg. than in one of 120 deg. There is a beneficial effect of air movement when the effective temperature of the environment is below the temperature of the body; above body temperature, air movement adds to the discomfort.[4]

If the temperature, humidity and air movement in a room are not of the correct value to dissipate the heat that our own bodies produce, we experience a sensation commonly termed "stuffiness." It is not the high carbon dioxide content or the absence of outside

air which causes this stuffy feeling in rooms which are not air conditioned. The fact was proven beyond a doubt by a very simple experiment, conducted by Dr. Leonard Hill in London, and is described in the Smithsonian Miscellaneous Collections, Volume 60, No. 23.

A number of people were placed in a hermetically sealed room. Tubes leading to the outside allowed them to breathe the outside air. Simultaneously, other people were placed outside this room and they were forced to breathe through tubes the air in the sealed room. The temperature and humidity of the air in the sealed room was gradually raised. Simultaneous observations were taken of the pulse rate, blood pressure, body temperature and comfort sensation of both groups. Those in the sealed room breathing outside air experienced all the usual symptoms and discomforts attributed to bad ventilation; and, as the temperature and humidity were increased, they had to be removed to prevent complete collapse. The others outside breathing the room air over and over again experienced no such symptoms and had no sensation of discomfort until long after the people inside the room had been removed.

This experiment exploded the old theories of the mystic effect of carbon dioxide and the toxic effect of expired air in the concentration normally found in unconditioned buildings. These theories were brought forth in the "Dark Ages" of ventilation to explain the very real discomfort experienced due to lack of air conditioning. A very high concentration of CO_2 such as might be experienced in a submarine will cause distress and eventually death, but the infiltration of air even into a very well-built room is so great that, in practice, such a concentration could never be produced in our modern buildings from the exhalation of the occupants.

Air movement plays an important role in air conditioning, not only because it blows away the warm and humid aerial blanket which surrounds the body, but also because it exerts a pleasant and stimulating effect upon the skin, a sensation lacking in still air. According to Baetjer,[23] who studied the influence of the air currents on comfort, "currents of air in the threshold of perceptibility contribute to our comfort in all probability by acting on the sensory nerves of the skin, directly or indirectly, and arouse sensations of an agreeable kind." Under ordinary room temperatures, she found that the perceptibility of air currents on the exposed surface of the body average about 4.5 ft. per minute.

In actual practice, Vernon[24] has shown that the output in British factories undergoes a distinct seasonal variation which varies inversely as the mean monthly outdoor temperatures. Unfortunately, he did not record the actual effective temperature conditions in the factories. Observations by Osborn and Vernon shows that the frequency of accidents in British munition factories reach a minimum at 67.5 deg. dry bulb temperature and that accidents increase above and below this temperature. Under more adverse conditions, such as those met at the Moro Velbo Gold Mine in Brazil, where the conditions averaged 101.5 deg. F. dry bulb and 87 deg F. wet bulb, twenty fatal accidents occurred in sixteen months prior to the installation of air conditioning equipment. During the sixteen months after the installation of air conditioning equipment, which lowered the dry bulb temperature to 76.2 deg F., only six accidents occurred and the output of the workers increased 12%.[26,27]

From investigations made by the Industrial Fatigue Research Board in the Coal Mines in England, it was found that the rate of production decreased from 100% at 65 deg. effective temperature to 59% at 81 deg. effective temperature, and the accidents increased from 78 to 137.[25]

The Philadelphia Electric Company has made a comparison of two of their District Offices which are similar in all respects except that one is air conditioned and the other is not. This analysis covered a period from September 1, 1932, to August 31, 1933.

During this period, the absences due to respiratory and other minor causes were 56% less at the conditioned offices than at the unconditioned offices.

They also made a study of the effect of air conditioning at their Main Office because they felt that after two years of operation a marked decrease in absences had occurred. To substantiate this, records of time lost due to sickness were classified as to the number of days lost and the causes thereof. Illnesses due to other than respiratory causes were not considered in this study.

The first comparison in the analysis was made of forty-five employees who had been in the office for one complete year prior to and one complete year after the air conditioning was installed. A reduction of 33% in lost time was noted. Continuing the analysis for the second year of conditioned air, they found a 46% reduction in lost time for respiratory causes compared with the year before air conditioning was installed.

The Eastman-Kodak Company conducted experiments on ventilation and a comparison of records for a year of good and a year of bad ventilation showed a 4% increase in output and a 50% decrease in illness in the ventilated plant.

It seems logical to assume that the applied science of conditioning the air in which we live, and which has such a tremendous effect on our health, comfort and efficiency, is as important a contribution to mankind as Pasteur's discovery of germs or the medical profession's development of the technique of sanitation, which have almost completely eliminated the epidemics which formerly desolated enormous areas of the world.

With the common use of air conditioning,[49,48,46] the control of other factors such as changing the chemical composition or varying the pressure may prove of value. Some research into the therapeutic value of changes in air pressure has been conducted. These indicate that an increase in pressure increases the oxygen tension in the air respired and thus increases the rate of its transfer to the blood stream. A decrease in pressure reduces the oxygen tension and stimulates certain organs to produce more blood cells and is of some value in the treatment of such impoverished blood conditions as anaemia. Possibly, the hospital or even the home of the future will have air conditioned rooms where the pressure can be increased to hasten the rate of metabolism and the repair of weary bodies of aged people; or be decreased to help the blood stream build up its red cells. This suggests the treatment of such diseases as tuberculosis by air conditioned trains, homes and offices instead of treatment by physical removal to more favorable climates.[44, 45,46, 47,48]

For some years the medical profession has controlled the chemical properties of the air by the use of oxygen tents in the treatment of pneumonia. With the installation of air conditioning in the hospital, it will be an easy matter to change the chemical properties of the air or to treat the air chemically, as soon as research and experience show us its therapeutic value.

The Effect on Illumination

Air conditioning has aided other advances in human comfort. The store, restaurant and office building of Yesterday were very inadequately lighted, according to our present day standards. The eyesight enjoyed by our forefathers has deteriorated with the development of

our modern civilization, and is probably accounted for by close work under inadequate lights. Modern lighting practice demands many times the wattage of Yesterday's standards and, even then, we have not reached the perfection that the illuminating engineer recommends. Yesterday, a lighting load of 1½ watts per sq. ft. was considered adequate. Now, 4 to 5 watts per sq. ft. is not an unusual lighting load. For display purposes, 10 watts is not uncommon and show rooms have been designed on the basis of 16 watts per sq. ft. In many of these cases, the heat from the lights alone is sufficient to heat the space to 70 deg. with an outside temperature of zero degrees—rather expensive heating, when considered only from that point of view! Such a lighting load used in mild weather, to say nothing of the hot summer, would raise the temperature of the room to a point where it would be uninhabitable. Ultimately, the illuminating engineer will produce a light or a glass shield which will give more illumination and less heat (and designed, undoubtedly, to give the proper proportion of the ultra-violet and other beneficial rays which are present in the sun's spectrum), but present illuminating practice has made air conditioning more of a necessity. Or, to put it another way, air conditioning has made good illumination possible.

Relation to Abatement of Noise

As air conditioning grew from the industries into the theatre, the broadcasting studio, the sound stage, the office building and the home, it was found that the noise level produced by the industrial design of air conditioning equipment was far too high. An air conditioning system permits the closing of the windows thus protecting the space being conditioned from the external noises such as we have in our cities today; and, under these conditions, the noise produced internally by the industrial air conditioning system was found in many cases to be objectionable.[29]

The problem of noise abatement is becoming more and more clearly associated with the problem of air conditioning. The public is becoming noise conscious. Investigations and researches by efficiency experts of leading corporations, by health authorities and by life insurance companies have demonstrated that noise is exacting a heavy toll in the reduced output of all types of workers, in worn and shattered nerves and in a shortening of the average span of life.

The amount of sound energy generated by the average speaker is

extraordinarily minute. A person in conversation generates only about 10 microwatts of speech energy. The average amount of speech energy generated by a speaker is about 25 microwatts in a small room and 100 microwatts in a very large auditorium. If it were possible to set up a pressure gauge in an auditorium which would be sensitive enough to measure the pressure variations in the air due to the vibrations of sound, such as are produced by speech, the root mean square pressure variation would be less than one-millionth of atmospheric pressure; but, if the acoustic conditions in the room are ideal, even these feeble vibrations will be recognized by the sensitive mechanism of hearing.

To gain a better notion of the loudness of speech, music and noise, it is necessary to define a suitable unit for measuring the intensity or loudness of sound. It has become more and more universal to rate the intensity of sound in terms of what is called the "sensation level," which is defined in terms of the sound which is just barely audible to a person with normal hearing.

This unit has been established. It is called a "decibel," and its formula is: $10 \log \frac{I_1}{I_0}$. I_1 is the average intensity of the sound to be measured. I_0 is the intensity of the same sound when it has been reduced to the point that it is just barely audible to a person with normal hearing. (The intensity is rated in terms of the number of microwatts of acoustical energy fluxing through an area of one square centimeter). If I_1 is a million times I_0—that is, if it is of such a magnitude that it is necessary to reduce its intensity one million-fold in order to reduce it to the threshold of audibility—its sensation level will be 60 decibels. (The common abbreviation of decibel is "db.")

The following examples give some idea of a decibel, or "db" in terms of the sensation level of familiar sounds:

Rustle of trees in a gentle breeze	10 db.
Soft radio music	35
Quiet office	37
Average office	47
Noisy office	57
Ordinary conversation	65
Very noisy stenographic department	70
Loud radio	80
New York subway	95
Riveting	98
Aeroplane motor, unmuffled	115

The average sensation level of speech in a small room is about

60 to 65 db., but in a large auditorium it drops to approximately 50 db., whereas the sensation level at which speech is most readily recognized is about 70 db. The articulation of speech drops off very rapidly with any further diminution of the intensity and, since 50 db. is about the average level of speech in a very large auditorium, it is obvious that it is at such a critically low level that any external noise would interfere very seriously with the hearing.

Actual tests have shown that a noise [28] of 50 db. will reduce speech articulation approximately 50%. These tests were conducted in such a manner that the speaker did not hear the noise. If the speaker as well as the listener hears the noise, the speaker will attempt to raise his voice above the level of the noise, and in this case the noise in the auditorium will not produce as great an interference. It follows that if there must be some noise in an auditorium, it is much better to have this noise in the proximity of the speaker than in the proximity of the listeners.

The acoustics of a room [29,30] of course depend very much upon the shape. Certain conditions may give rise to sound reflections which, if delayed as much as 55 ft. behind the direct sound, will interfere with the direct sound; and if delayed as much as 65 to 70 ft., will be heard as an echo of the direct sound. Again, a large room bounded by highly reflective surfaces may give trouble due to reverberation caused by successive reflections from the boundaries of the room. In some cases, the reverberation of an ordinary sound may remain audible for fifteen seconds.

In designing an air conditioning system, we are concerned primarily with the elimination of the sound produced by the equipment used. A quiet operating fan and motor will have a noise level as high as 65 db., and this noise level of course would be highly unsatisfactory in an auditorium, an office or a home. The amount of noise, measured in terms of decibels above minimum audibility, which can be tolerated in various rooms is as follows:

Studios for the recording of sound, as talking picture studios	6 to 8 db.
Radio broadcasting studios	8 to 10 db.
Hospitals	8 to 12 db.
Music studios	10 to 15 db.
Apartments, hotels and homes	10 to 20 db.
Theatres, churches, auditoriums, classrooms and libraries	12 to 24 db.
Talking picture theatres	15 to 25 db.
Private offices	20 to 30 db.
Public offices, banking rooms, etc.	30 to 40 db.

These values represent what might be termed "ideal conditions" and if they are not realized in existing buildings there is no occasion to design an air conditioning system with a lower noise level. It can be readily seen from the formula of a decibel that the introduction of an additional sound of equal acoustical energy will only increase the sound or sensation level ten times the log to the base 10 of 2, which is 3.01 decibels. The average human ear does not notice appreciably a variation less than 5 db. in sound level; therefore, the introduction into a room of another sound of equal intensity to the prevailing sound level will not be objectionable.

The air conditioning engineers have discovered methods of making the apparatus itself much quieter and have developed sound absorbers which effectively eliminate the transmission of sound that remains. On certain sound stage and broadcasting studio installations, air conditioning engineers have worked against the absolute zero of sound, which is considerably below minimum audibility. In other words, they have eliminated sounds which, although unnoticeable to the human ear, are detected by the sensitive microphones and amplified by the radio broadcasting system to a point where they would have interfered with proper radio transmission.

Although the human ear can detect noises of frequencies ranging from 30 to 16,000 cycles per second, fortunately most noises have their maximal sensation level between 512 and 1024 cycles per second, so that if the sensation level of the noise is determined in this range one will have a measure of the noise which is sufficiently accurate for most engineering purposes.

There are three accepted methods of measuring the intensity of sound:

First—The tuning fork method.
Second—The audimetric method.
Third—The acoustimeter method.

The tuning fork method is extremely simple, and gives satisfactory results if used with proper care. It is advisable to use at least three forks, tuned to 128, 512 and 2048 cycles. The rate of decay and the intensity in db of the fork after it has received a standard blow is first determined. The fork is struck a standard blow in the presence of the noise to be measured. It is then held in front of the ear and observations made of the number of seconds which elapse before the tone of the fork is masked by the noise. For instance, if a fork has

an initial intensity of 66 db and a tone decay of 1.1 db per second, and if the noise masks it in 20 seconds, then the noise level is 66 db minus (20×1.1), or 44 db.

The buzzer type of audiometer is a somewhat similar but much more convenient method of determining noise measurement. The buzzer in this audiometer has a fundamental frequency of 160 cycles, with an abundant supply of overtones, so that its noise is quite representative of most noises produced by air conditioning equipment. The observer first determines the amount of attenuation, in decibels, which must be introduced in the audiometer to reduce the buzzer sound to inaudibility when listening in a perfectly quiet place. He then makes a similar measurement when listening in the presence of the noise which is to be measured. The difference in the two readings of the audiometer gives a measure of the masking effect of the noise which, as measured by the threshold shift, is about 5 to 10 db less than the sensation level of the noise.

In the acoustimeter method of measuring noise, the noise vibrations are picked up by a microphone, amplified by a vacuum tube amplifier, passed through a frequency weighting network, then registered by a galvanometer. The frequency weighting network must be based upon the sensitivity and sensibility characteristics of the normal human ear and, if so, the deflections registered by the instrument will be comparable to those which would be heard by the ear. This method gives fairly reliable results, but the effect of the frequency weighting network is to introduce certain errors due to variations of the intensity and frequency distribution in the noise to be measured.

Design Problems of Air Conditioning

An air conditioning system introduces many problems in air distribution which are not experienced in the design of ventilating systems. A ventilating system is generally designed to deliver air either at room temperature or sufficiently above room temperature to heat the room. In the design of a warm or tempered air ventilating system a great deal of care must be taken to eliminate drafts. Observations showed that drafts were seldom experienced at exhaust outlets and invariably appeared at the supply outlets. Therefore in many designs of ventilating systems the maximum number of supply outlets, placed if possible at points where drafts would not be objectionable, and a multiplicity of return air openings were installed. This mini-

mized the trouble due to drafts—at the expense of good distribution—and this method grew to be quite common practice.

The advent of the use of cooled air for air conditioning, with its heavier density and its tendency to fall rapidly to the floor, immeasurably increased the difficulties of preventing drafts. Using the stopgap of increasing the number of return openings at the expense of the supply openings only demonstrated too clearly the faulty distribution of this method of air circulation. It was clearly evident that good distribution could be obtained only by an adequate number of supply outlets, and if these were placed correctly the location and number of the return openings would be relatively less important.

The proper use of cooled air introduces another problem. To produce a desirably low relative humidity, the psychrometrics of the air demand that it be cooled in summer to 50 deg. or below to keep the dew point of the air at the proper point. Therefore, to maintain a room temperature of 75 deg., air 25 deg. below room temperature must be introduced through the supply outlets. The heat absorbing capacity of air rising through 25 deg. is too great in most cases to permit of sufficient air being circulated to give adequate distribution. If the differential were lowered to permit more air circulation, the dew point of the entering air would be raised, with the result that the relative humidity in the room being conditioned would be far too high. To cool the air to 50 deg. and then re-heat by steam or some other external source of heat seemed to be the only solution, though unsound both economically and thermodynamically.

Air conditioning engineers have obtained the solution of this problem. They discovered that the construction of a by-pass around the cooling medium and the taking of a portion of return air through this, would solve the problem. This permitted the cooling of the proper amount of air by the cooling medium to the correct dew point and increased the air circulated to the amount necessary for good distribution. The differential between the supply air and the room temperature was reduced to the point where there was no danger of drafts. This method required less than 75% of the refrigeration which would otherwise have been necessary. The development of this so-called "by-pass" method was a very vital and important contribution to the art of air conditioning.

Other recent developments have been along the line of distribution of the air. The architect has constantly increased the lighting load in

the modern building, and thus has increased considerably the amount of air necessary to condition it properly. In addition, he has demanded that the air be introduced through outlets which are inconspicuous and which harmonize with the architectural design. The combination of outlets with lighting fixtures has proved to be a very happy solution from the standpoint of many architectural designs. Other outlets have been developed consisting of narrow slots operating at comparatively high pressures, which can be fitted into the architectural design. A few years ago, it was a foregone conclusion that an outlet with a velocity of 400 feet per minute or more would be noisy and drafty. Today, outlets have been designed and are in actual operation with outlet velocities of 2,000 feet per minute, and these are absolutely noiseless and draftless. The development of such outlets permits the use of much smaller ducts, thus increasing the head-room and reducing the cost of the investment.

Source and Nature of Heat Load

In designing an air conditioning system for cooling, the heat load must of course be studied. In the main this load is produced by the power expended by the machinery in the rooms, the people, the lights, the transmission through the walls due to the difference between the inside and the outside temperature, infiltration and the radiant heat from the sun. Depending upon the type of building, any one of these may constitute the major load and, if so, this may radically affect the design of the system. For example, a theatre in which the major load is people will require a different type of system from a textile mill with its major load of power, or a sound stage with its large lighting load, or an office building where the radiant heat from the sun is the largest factor to be considered—although in all these cases the total heat load may be the same.

Each of these sources of heat deserves investigation. One horsepower of mechanical energy liberates 42.5 btu per minute into the space in which the energy is expended and if the motor driving the machine is also in the room, we must consider the kilowatt input of the motor and not the brake horsepower used by the machine.

The form in which the heat is produced must also be studied. For instance, approximately 65% of the heat produced by the ordinary electric light bulb appears as radiant heat, 10% in the form of light which is transposed into heat when it strikes an object, and the remaining 25% is dissipated by convection and conduction.

The human body produces both sensible and latent heat. Latent heat appears in the form of perspiration and evaporation of moisture from the lungs. The total amount of heat varies with the room temperature and with the amount of work being done; and the relation of latent to sensible heat changes, depending upon the temperature of the room and the work a person may be doing. In this connection, such diversions as dancing will of course have to be considered as work.

The total body heat produced at ordinary room temperature is 400 [10,52] btu per hour when at rest, and 850 btu (Figs. 10, 11) per hour hour when doing 33,075 foot pounds of work per hour. The latent heat, or perspiration increases with the work done much more rapidly than the sensible heat. For people at rest, the total heat ranges from 525 btu per hour at 45 deg. effective temperature to zero at 100 deg. effective temperature, but is practically constant between the effective temperatures of 64 and 78 deg. The relation of latent to sensible changes quite rapidly (Figs. 12, 13, 14, 15, 16). At 70 deg. dry bulb (Figs. 17, 18), for people at rest with an air velocity of 25 ft. per minute, the sensible heat is 5.12 btu per minute; at 80 deg. dry bulb, it is 3.74 btu per minute. At 70 deg. dry bulb the latent heat is 1.58 btu per minute; at 80 deg. dry bulb, it is 2.86 btu per minute. (Fig. 19).

The proportion of the sensible heat lost by radiation [50] is also of importance. This varies with the air velocity and the wall temperature. The proportion of sensible heat lost by radiation at an air velocity of 190 ft. per minute is approximately one-third of what it is at zero velocity. It is twice as much with a wall temperature of 15 deg. C.[37] as it is when the wall temperature is 26 deg. C.

Air Motion Ft. per Minute	Total bodily radiation in Per cent of Sensible Heat
0 ft. per min.	60%
75 ft. per min.	41%
135 ft. per min.	35%
190 ft. per min.	25%

Wall or Air Temperature	Total bodily radiation in Per cent of Sensible Heat
25.6 deg. C.	66%
24.1 deg. C.	75%
21.3 deg. C.	80%

The radiant heat from the sun [35] requires close study, as it is the largest single factor in the design of air conditioning systems for homes, office buildings or factories in which the power consumption is relatively low. The sun's temperature is estimated to be 10,800 deg. absolute. The solar radiation on a surface normal to the sun above the atmosphere is approximately 425 btu per sq. ft. per hour. However, the absorption of the upper atmosphere and the water vapor, dust and smoke in the lower atmosphere reduces this in clear weather to an average of 253 btu at sea level, although values as high as 338 btu have been reported. Probably 300 btu per sq. ft. per hour would be a conservative value to figure. The temperature of the sky ranges from 80 deg. F. in the daytime in summer to minus 40 or minus 50 deg. F. on a clear evening after sunset.

The solar radiation on horizontal roofs or vertical walls varies of course with the latitude, the time of the day and the orientation of the walls. In a latitude of 40 deg. north on August 1st (Figs. 20, 21, 22), the east and west walls reach a maximum of 210 btu per sq. ft. per hour. The east wall reaches its peak in the morning, the west wall in the afternoon. The curves are quite steep and the peak is of a duration of approximately three hours. Solar radiation on the south wall has a peak of 120 btu per hour, but the curve is comparatively flat. A horizontal roof will reach a peak of 275 btu, with a fairly flat curve, the duration of the peak being approximately six hours.

The temperature of surfaces [34,36,37,41] heated by solar radiation is of course influenced by the nature and color of the surface. Neglecting convection, conduction and re-radiation, a temperature of 425 deg. F. is theoretically possible. Actually, convection, conduction and re-radiation to the sky reduce it to a theoretical high of 233 deg. Temperatures as high as 170 deg. F. have been recorded on black roofs and black tar pavements.

Schropp measured the surface temperatures of different materials [36] exposed to perpendicular solar radiation at different seasons in Germany. The materials, in the form of a thin plate, were located on a 2-inch thick cork plate. Such an arrangement corresponds to the heat insulation of a well-insulated roof. During the time of solar radiation with still air, the increase of surface temperature above the outside air temperature was: For a black surface, 81 deg. to 99 deg. F.; for aluminum sheet (rough), 54 deg. to 63 deg. F.; for a white surface, 27 deg. to 36 deg. F.; for glossy aluminum foil, 27 deg. F.

The temperatures increase progressively with the relative blackness of the color as was noted for King's results.

The flow of solar [38,31,32,33] radiation through a wall or roof on a hot day is very complex. It may be illustrated in Figure 23, where "XY" is the roof or wall structure.

The intensity of impingement on the surface, "X," not normal to the sun's rays, decreases with the angle of incidence, "I," which is a function of time; a part of the energy, "B," is not absorbed, but is

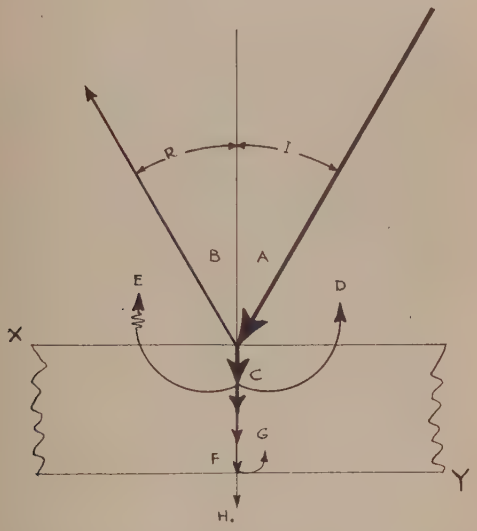

FIG. 23. Factors affecting heat flow through roof of walls.

reflected away. The magnitude of "B" is a function of the character of the surface, "X," and of the angle of reflection, "R," which varies with the time of day. The remaining energy, "C," is absorbed as heat by the surface, "X," raises its temperature enough to cause the radiation, "D," back through the air, and the convection loss, "E," by direct contact with the air. Also, as the temperature of the surface, "X," is raised by the absorption of radiant energy, heat flows in the direction, "F." As the temperature of the surface, "X," rises to a maximum at noon and then recedes, a wave of heat advances towards "F." Because heat is required to raise the temperature of each increment of the dis-

tance, "X" to "Y," the rate of heat flows past any point between "X" and "Y" diminishes as the wave penetrates through the structure, and when the wave reaches the surface, "Y," it has a much lowered amplitude, dependent upon the conductivity, density, specific heat and thickness of the material in the wall, the film resistance of its lower surface and the temperature of the air below. The crest of the wave reaching the surface, "Y," will be delayed a certain time after the crest at the surface, "X."

The heat reaching the lower surface tends to build up its temperature and a small amount of heat, "G," returns in a reflected wave upward towards "X." The magnitude of this reflected wave also depends upon the physical properties of the structure. Only "H," the heat entering the air conditioned space below, is of interest to the air conditioning engineer.

Conductivity, density and specific heat are factors which combine to damp out the wave amplitude. In a theoretical consideration of heat transfer they are combined into a single constant (h), called the diffusivity:

$$h = \sqrt{\frac{k}{cp}}$$

where

h = diffusivity
k = conductivity
c = specific heat
p = density

This combined constant takes into account the resistance to heat flow and the heat capacity of the structure.

It follows, therefore, that the walls of such structures affected by solar radiation experience a periodical heat flow phenomenon, and that the temperature variation is less pronounced and lags the diurnal and annual variation of the surrounding atmosphere.

In other words, the mass of the structure acts as a fly-wheel and has a tremendous influence in reducing the peak loads imposed by solar radiation. This also has the effect of preventing a very rapid reduction of the temperature in a building after a hot spell, as the mass will give off its heat at a much slower rate than it will absorb it, due to the difference in temperature heads.

Ordinary [40,42] window glass will reduce the solar radiation by approximately 10%. Window shades of different reflecting powers also will reduce the effect of the sun's radiation on the air in the room. However, the effect of window shades is not caused by re-radiation out the window, as ordinary window glass absorbs all heat rays at a temperature of red heat or below. The heat absorbed by the window glass is in turn transmitted to the walls by conduction and thus absorbed by the building mass. The use of awnings will very appreciably reduce the amount of solar energy transmitted, but they do not exclude radiant energy reflected from the surroundings.

Experiments [39] have been made with glass that will transmit the visible light of the sun and exclude the invisible ultra-violet and infra-red rays. Approximately 56% of the sun's energy is in the invisible part of the spectrum, 44% in the visible, as shown in the table below:

Spectral Range A	Per cent of Total Solar Energy	Btu./ft.²/hr.
2,900—4,000	3.9	11.7
4,000—7,600	43.7	131.1
7,600—	52.4	157.2
Total	100.0	300.0

However, such glass becomes quite hot, due to the large amount of energy absorbed and is therefore subjected to severe temperature shocks. Some of the heat absorbed by the glass of course finds its way into the room through re-radiation and convection, so that this glass should for maximum effect be used in a double window with ordinary window glass inside. Such a window will transmit 62% of visible light compared to 92% for ordinary glass, and exclude 63% of the total solar energy compared to 12% for ordinary windows.

The transmission [43] through the walls of the air conditioned room due to the difference between the inside and the outside temperature is generally of small importance, as the temperature differentials are not high. We will not discuss these here, as these factors have been fairly well established in heating practice.

Infiltration of course may have a large effect, depending upon the tightness of the doors and windows and their relative proportion to the total cubical content. The curves (Figs. 24, 25) shown below give some indication of this effect.

All these factors must be evaluated and properly weighed before the size and type of equipment can be selected.

Typical Air Conditioning Equipment

Many designs of equipment have been produced to meet the varied and increasing demands for air conditioning. An air conditioning unit (Fig. 26) which takes the place of the ordinary direct or indirect radiator and which can be located in the same position underneath the windows, has been used successfully in a number of installations. This unit is supplied with conditioned air through small vertical ducts located in the pilasters adjacent to the outside columns. These ducts are so small that they take little, if any, rentable space. Figure 27 shows the schematic arrangement of such a system. Research indicates that the further development of this method will probably be the ultimate solution of air distribution in multi-story hotels, apartment houses and office buildings. The development will probably be in the direction of increasing the air and outlet velocities. The future air conditioning system may discard the present galvanized iron ducts and use steel or copper pipe for the movement of air at high velocities and pressures.

Figures 28 and 29 show the schematic arrangement of an air conditioning system for a multi-story office building, using two different methods of distribution. Due to the diversity of the loads, two complete separate systems were used. One system, consisting of two refrigerating machines and seven dehumidifiers, was used to take care of the first five floors of the building where the load was chiefly lights and people, with relatively no sun effect. The office tower of the building from the 6th to the 33rd floors was conditioned with a completely separate system, consisting of two refrigerating machines, with two dehumidifiers on the 20th floor supplying air through vertical shafts to two individual re-circulating fans located on each of the twenty-five floors. All these fans distribute air through ducts concealed by plaster on the ceiling of each of the floors. One cooling tower on the roof furnishes condenser water for all four refrigerating machines.

Figures 30 and 31 show a centrifugal refrigerating machine, which is quite commonly used for this type of work. This machine uses dichloromethane (CH_2Cl_2) as a refrigerant. This refrigerant is efficient and is harmless, non-combustible, non-explosive, liquid at atmospheric pressure under normal temperature conditions. Both the high and low side of this machine are below atmospheric pressure. The inherent characteristics of a centrifugal compressor, with comparatively high efficiency at partial loads and its automatic adjustment to

these conditions, are particularly adapted to an air conditioning load which, dependent on the weather, is of a highly fluctuating nature.

This centrifugal machine is compact and occupies less than one-quarter of the space required by a reciprocating machine. As space for equipment in a commercial building is generally at a premium, or often drastically limited, this is quite an important feature.

This machine is simple in operation and costs little to maintain, as it has very few wearing parts. As its speed of rotation is 3500 RPM or more, it is ideally suited for steam turbine drive, although the most usual drive is by electric motor.

Other new refrigerants have been discovered. The most familiar of these is F-12 or Freon, chemically dichloro-difluoromethane, with a chemical formula of C Cl_2F_2. This refrigerant is non-explosive and non-inflammable, and is practically harmless at room temperatures. Due to its small specific volume and large ratio of compression, in the ordinary commercial sizes it is not adaptable for use with centrifugal compressors, and positive compression machines of the reciprocating type have been developed for its use.

Other refrigerants are being experimented with in the chemical research laboratories, and others such as Zeron, which is adaptable to centrifugal refrigeration, and is more efficient than dichloromethane for evaporator temperatures ranging from 15° F. to zero and below, is being used today in actual plant operation.

Due to the dangerous characteristics of ammonia gas, and due to the inefficiency and other disadvantages of CO_2 as a refrigerant, F-12 will probably replace them for use in the air conditioning field except in the larger sizes, where the centrifugal machine has certain obvious advantages.

The old Le Blanc process, which uses water as a refrigerant by producing a vacuum which causes the water to boil at temperatures as low as 34 deg., has been given new life. This process, patented in the 19th Century, was brought to this country years ago from France and discarded because of the development of other refrigerating systems which were more economical. Today, our improved knowledge of the design of the steam nozzle (Fig. 32) has permitted us to obtain steam economies which give this method a real place in the air conditioning field where it is not necessary to cool water below 40 deg. Its one disadvantage is that the necessary condensation of the steam requires three to three and a half times the amount of condenser water as that

used by a compression system. This will limit its application to the smaller sizes. In the larger sizes, where the use of steam is indicated, a centrifugal refrigeration machine driven by a steam turbine will show a sufficient saving in steam and condenser water consumption to more than pay for its slightly higher first cost, unless cheap steam is available at fairly high pressure and there is an unlimited supply of cheap condenser water.

The use of steam for cooling in the summer provides a much needed summer load for the public utility which is distributing steam for heating during the winter.

Some ingenious engineers have discovered that it is possible to heat a house with a refrigerating machine. They reversed the refrigerating cycle and used the condenser as a heating medium. The coefficient of performance of this so-called "inverted refrigeration" is defined as the ratio of the total heat delivered to the building divided by the heat equivalent of the electrical energy consumed by the plant. Strange as it may seem, this coefficient of performance, based on the Carnot cycle, theoretically may be as high as 5.8. Practically, the superheating of the vapor and the mechanical inefficiency will reduce the coefficient to at least 2.4. That is, for 1 btu supplied as electrical energy, 3.4 is available to heat the building. The initial and the operating cost of this system is generally higher than the conventional air conditioning system, but there are districts where the electric power rate is low enough to make this system practical. Its application is also limited to those sections of the country where the winters are mild. Theoretically, this system has possibilities, especially if a variation of the Carnot cycle is applied; and the experiments of the future may develop it into a more practical and common use.

In certain cases, where first cost is of primary importance of where the use factor is very low, as in a church or lodge-room, artificial ice has its field. Many ice melting units have been developed to supply this demand. The railroads have used them to pre-cool and to cool their cars, pending the improvement in business conditions which will permit them to finance the cost of mechanically air conditioning their entire passenger equipment. Except under such special circumstances, the present higher operating cost of ice melters more than neutralizes their smaller capital investment.

The air conditioning manufacturer realized that the gas companies were searching for a summer load for their gas, the consumption of

which reaches a very low valley in the summer months. They have developed an air conditioning unit for the home and small commercial spaces which obtains its energy from the consumption of gas; and, of course, the air conditioning engineer has not overlooked the use of oil and automatic coal stokers in designing his apparatus.

Until recently, most air conditioning systems have been custom-made installations (Figs. 33 and 34). Naturally, such a system does not lend itself to production methods and the cost is comparatively high. The manufacturers of air conditioning equipment realized that before air conditioning would come into general use, their cost would have to be lowered considerably and they have been working for some time on standard units (Figs. 35, 36, 37, 38) which would lend themselves to production methods. For a small room or office, there has already been developed a complete, packaged air conditioning unit (Fig. 39) which can be installed with a minimum of cost.

Present Stage of Art and Its Future

Air conditioning has made terrific strides. It is a recognized part of the manufacturing process of some two hundred different industries. It is traveling; we find it on the trains. It is sailing the seven seas with the modern steamships. We find it in the bowels of the earth, in the deep mines of Brazil and South Africa. It is gone into Government; we find it in the White House, Senate, House of Representatives and the Supreme Court. We find it at home, and many other places too numerous to mention.

The buildings erected today and tomorrow without air conditioning will be obsolete in five years. Air conditioning is sound from every angle from which it can be analyzed, and it will soon be incorporated in every building and residence of any importance.

Future of Air Conditioning and the Problems It Will Raise

The future air conditioning installations will place tremendous power loads on the lines of the public utilities, and it will be a particularly attractive load as its summer peak will come at the time when they most need the load. It should be a large factor in reducing the future cost of power, for its summer peak will increase the load factor of the central power plant. It may even transform the present summer valley into a summer peak. The progressive power companies

are well aware of its possibilities, have already made surveys and are watching this new industry intently, so that they may be certain to have sufficient power available to take care of its needs. This future load, not including the tremendous possibilities in the residential field, has been estimated to be 2,200,000 connected horsepower, with an average yearly consumption of 1,750,000,000 kilowatt hours.

Air conditioning, in addition to power, requires condenser water. Fundamentally, a refrigerating machine is a heat pump; that is, all it does is raise the heat load to a point where this heat can be dissipated by air or water at the temperature available. The supply of sufficient condenser for the air conditioning need of the buildings within a modern city presents a serious problem. Cooling towers can be used. They are practical and fairly efficient, but their use on any large scale would involve serious engineering problems, especially in erected buildings. Thermodynamically, a cooling tower absorbs all the latent and sensible heat from the space that is being cooled, together with the heat of compression, and dissipates that heat into the atmosphere in the form of latent heat. A great concentration of these cooling towers would not make the outside air of the cities in which we live any more endurable, and their use is probably not the final solution of the problem.

Possibly in those cities which are situated near rivers, the problem will be met by piping raw river water through the streets to supply condenser water to the buildings which need it. Possibly the final solution will be the development of air conditioning as a public utility. Where concentrated air conditioning loads develop, central refrigerating plants can be constructed near convenient sources of condenser water, and these refrigerating plants can pipe cold water through the streets just as steam is delivered to our doors today from central steam plants.

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APPENDIX

to

The Development of Air Conditioning in Industrial, Residential and Public Buildings; Its Effect on Human Beings; The Factors Which Enter into its Design

By

P. L. Davidson

Contents

18 Photographs

13 Curve Sheets

3 Tables

4 Diagrams

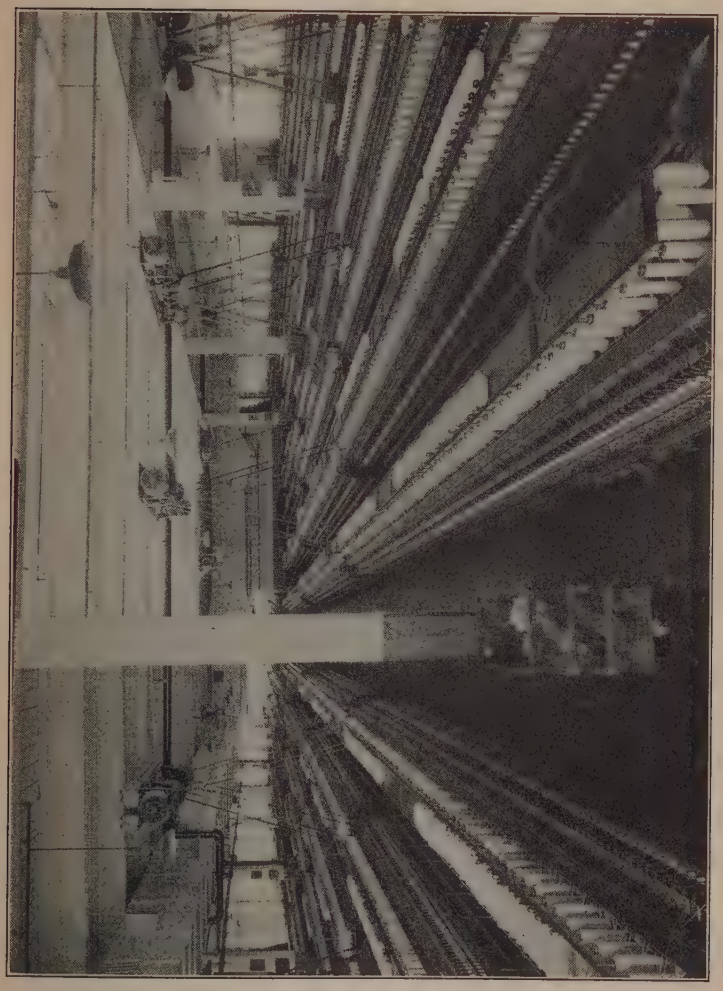

Fig. 1. Cotton Spinning.

Fig. 2. Cotton Weaving.

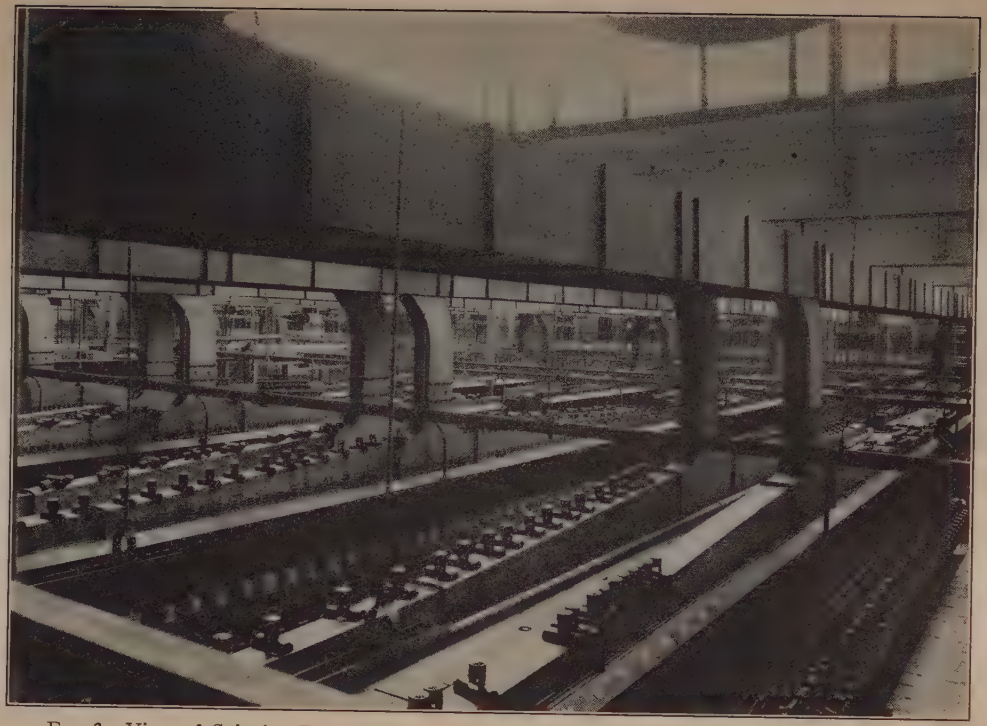

FIG. 3. View of Spinning Department in a rayon manufacturing plant (viscose process) showing maze of air ducts and pepper-box distributing ducts over each spinning machine.

FIG. 4. Viscose Process Sorting Room.

FIG. 5. Hand Rolling Cigars.

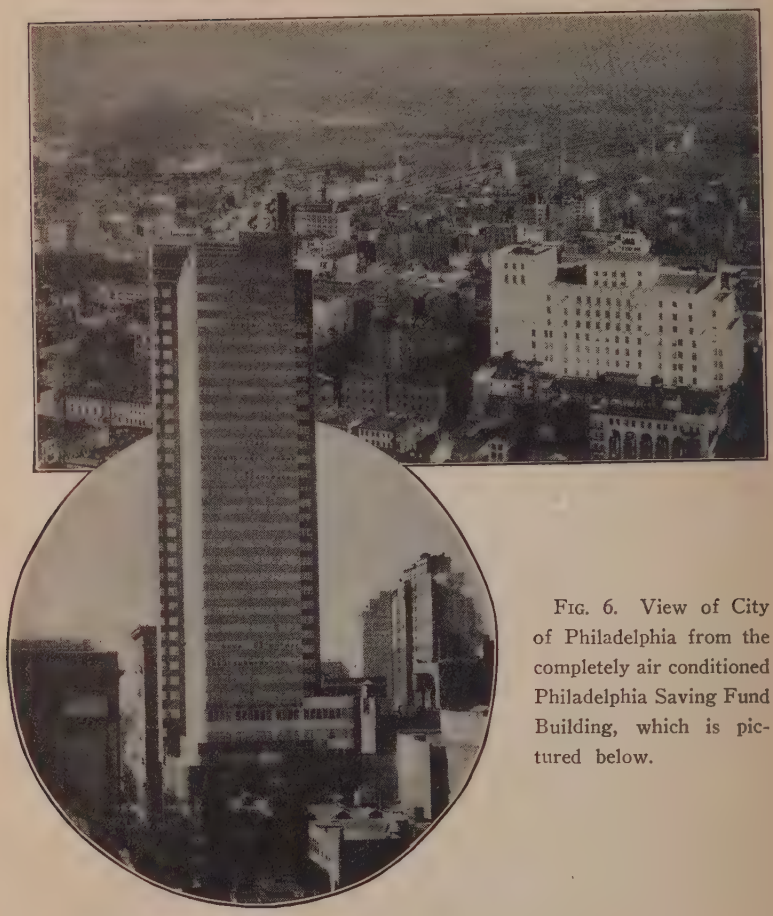

FIG. 6. View of City of Philadelphia from the completely air conditioned Philadelphia Saving Fund Building, which is pictured below.

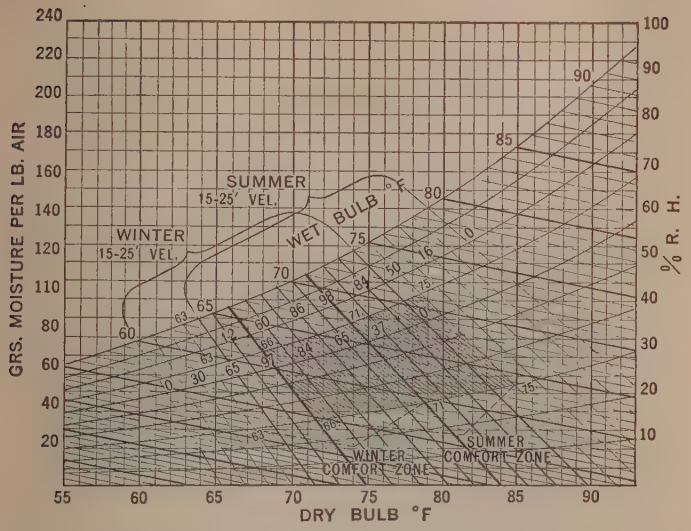

Fig. 7. Psychrometric Chart with accepted winter and summer comfort zones superimposed.

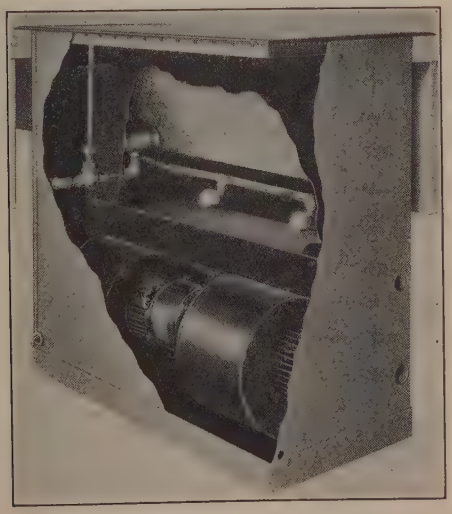

Fig. 8. Target type Home Humidifier.

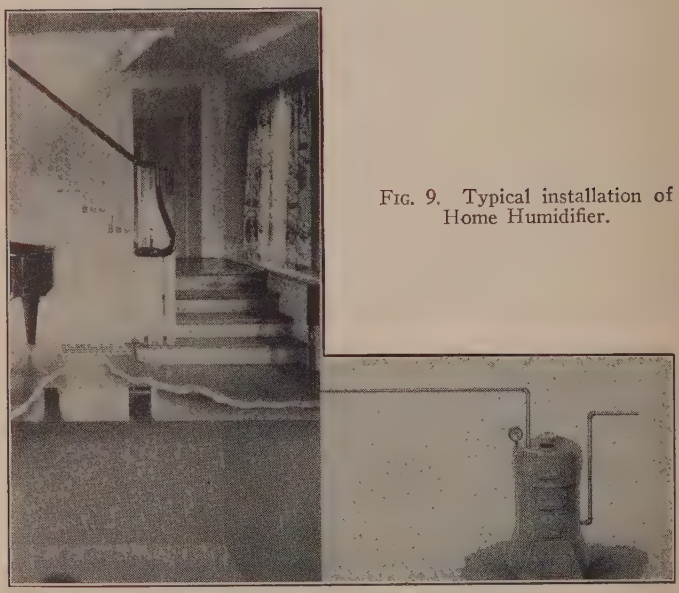

FIG. 9. Typical installation of Home Humidifier.

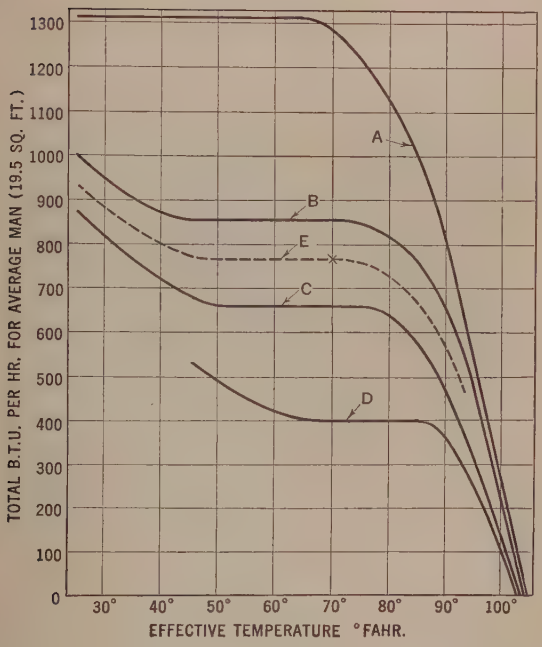

FIG. 10.52 Relation between total heat loss from the human body and effective temperature for still air.*

* Curve A—Men working 66,160 ft.-lb. per hour. Curve B—Men working 33,075 ft.-lb. per hour. Curve C—Men working 16,538 ft.-lb. per hour. Curve D—Men seated at rest. Curves A and C drawn from data at an effective temperature of 70 deg. only and extrapolating the relation between curves B and D, which were drawn from data at many temperatures.

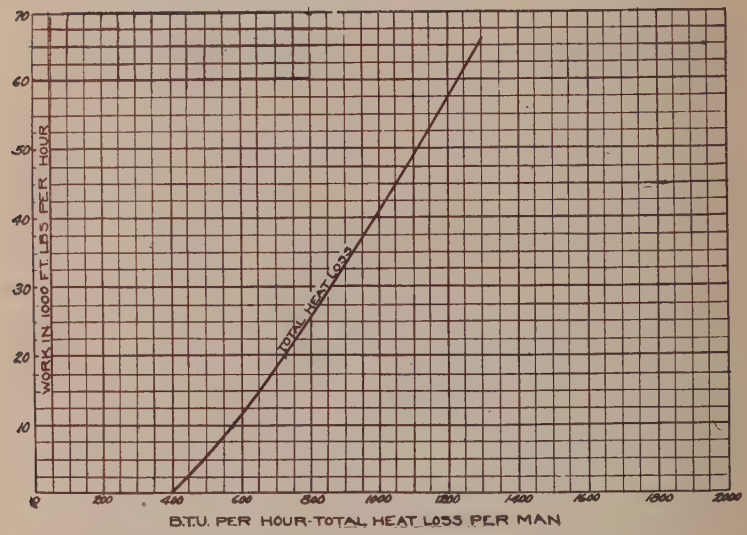

FIG. 11.52 Total heat from human beings at work, still air.

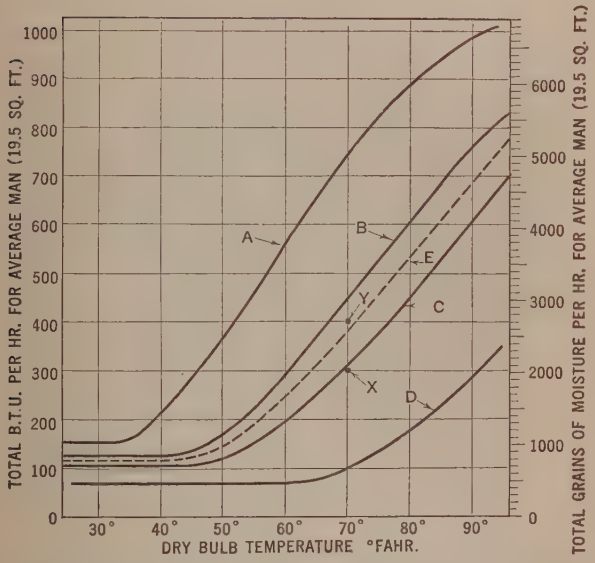

FIG. 12.[52] Latent heat and moisture loss from the human body by evaporation, in relation to dry bulb temperature for still air conditions.*

* Curve A—Men working 66,150 ft.-lb. per hour. Curve B —Men working 33,075 ft.lb. per hour. Curve C—Men working 16,538 ft.-lb. per hour. Curve D—Men seated at rest. Curves A and C drawn from data at a dry bulb temperature of 81.3° F. only and extrapolating the relation between curves B and D which were drawn from data at many temperatures.

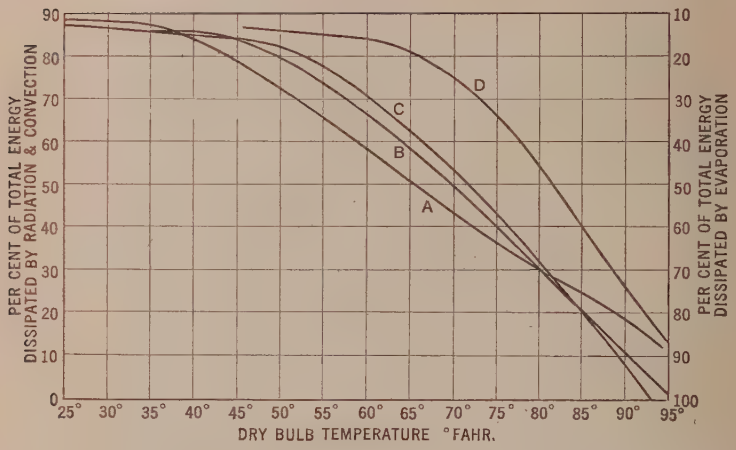

FIG. 13.52 Heat loss from the human body by evaporation, radiation and convection in relation to dry bulb temperature for still air conditions.*

* Curve A—Men working 66,150 ft.-lb. per hour. Curve B—Men working 33,075 ft.-lb. per hour. Curve C—Men working 16,538 ft.-lb. per hour. Curve D—Men seated at rest. Curves A and C drawn from data at a dry bulb temperature of 81.3° F. only and extrapolating the relation between curves B and D which were drawn from data at many temperatures.

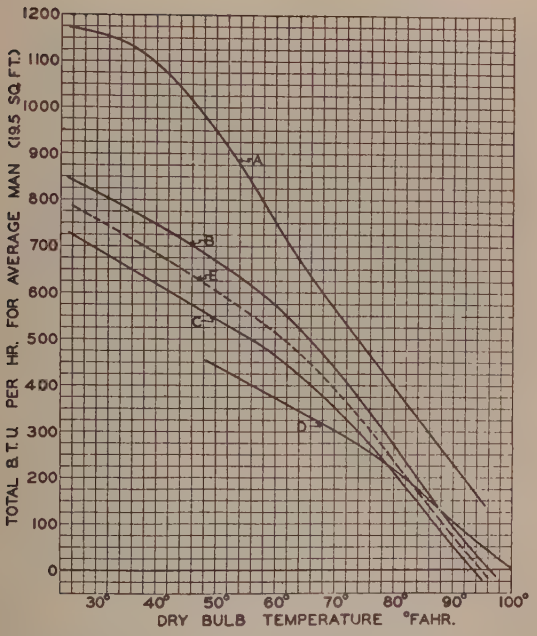

FIG. 14.[52] Relation between sensible heat loss from the human body and dry bulb temperature for still air.*

* Curve A—Men working 66,150 ft.-lb. per hour. Curve B—Men working 33,075 ft.-lb. per hour. Curve C—Men working 16,538 ft.-lb. per hour. Curve D—Men seated at rest. Curves A and C drawn from data at a dry bulb temperature of 81.3° F. only and extrapolating the relation between curves B and D which were drawn from data at many temperatures.

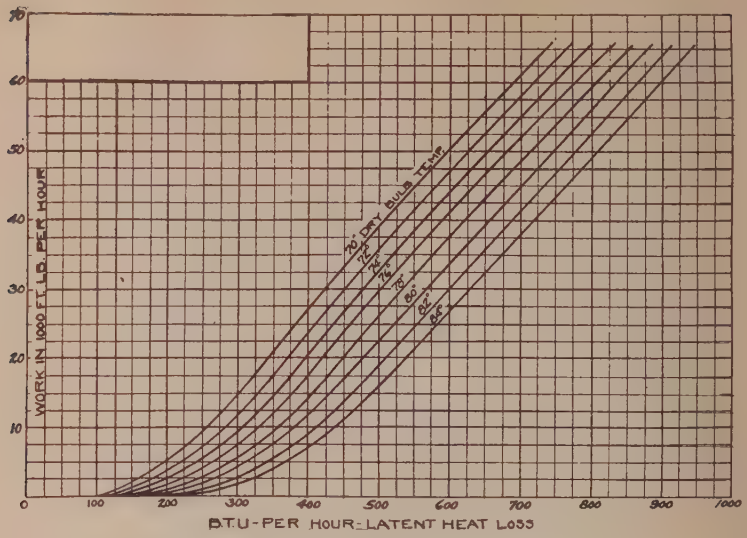

FIG. 15.[52] Latent heat from human beings at work, still air.

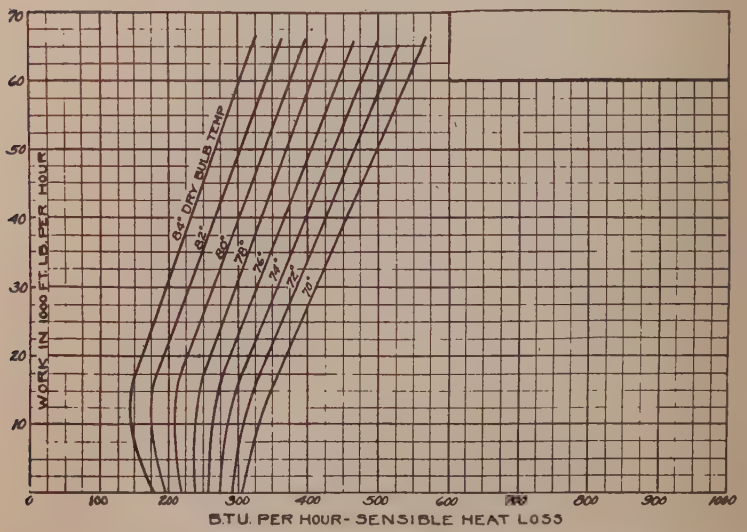

FIG. 16.[52] Sensible heat from human beings at work, still air.

HEAT LOSS IN B. T. U. PER MINUTE												
ROOM DRY BULB TEMP.	AT REST		10,000 FT. LB		20,000 FT. LB		30,000 FT. LB.		40,000 FT. LB.		50,000 FT. LB.	
	S. H.	L. H	S. H.	L. H.	S H.	L. H	S. H	L H	S. H.	L. H.	S. H	L H.
70	5.12	1.58	5.55	4.28	6.17	5.67	6.95	7.13	7.72	8 59	8.33	10.00
71	5.02	1.68	5 37	4.38	5.95	5.95	6.75	7.35	7.32	8.95	8.25	10.28
72	4.88	1.80	5.17	4.70	5.75	6.22	6.50	7.50	7.17	9.03	7.83	10.50
73	4.78	1.88	4.92	4.92	5.50	6.42	6.25	7.78	6.95	9.25	7.67	10.70
74	4.63	2.03	4.75	5.13	5.25	6.58	6.05	8.08	6.75	9.35	7.33	10.97
75	4.50	2.15	4.58	5.33	5.08	6.83	5 79	8.25	6.50	9.72	7.08	11.17
76	4.37	2.28	4.37	5.50	4.78	7.00	5.55	8.50	6.16	9.92	6.87	11.38
77	4.22	2.41	4.17	5.67	4.58	7.25	5.29	8.66	5.92	10.22	6.62	11.67
78	4.07	2.55	3.95	6.00	4.37	7.50	5.00	9.00	5.67	10.42	6.33	12.03
79	3.92	2.70	3.75	6.17	4.06	7.78	4.75	9.25	5.42	10.70	6.12	12.37
80	3.74	2.86	3.50	6.37	3.83	7.97	4.50	9.53	5.09	11.08	5.78	12.63
AT REST CONDITION IS BASED ON 25 FT. PER MIN. AIR MOVEMENT												

FIG. 17. Sensible and latent heat from human beings at rest and at work.

ROOM DRY BULB TEMP.	SENSIBLE HEAT B.T.U. PER HOUR PER OCCUPANT	SENSIBLE HEAT B.T.U. PER MINUTE PER OCCUPANT	GRAINS OF MOISTURE PER HOUR PER OCCUPANT	GRAINS OF MOISTURE PER MINUTE PER OCCUPANT	SENSIBLE HEAT PER MIN. PER 1000 OCCUPANTS	GRAINS OF MOISTURE PER MIN. PER 1000 OCCUPANTS
70	307	5.12	650	10.9	5120	10,900
71	301	5.02	700	11.7	5020	11,700
72	293	4.88	750	12.5	4880	12,500
73	287	4.78	790	13.2	4780	13,200
74	278	4.63	830	13.8	4630	13,800
75	270	4.50	890	14.8	4500	14,800
76	262	4.37	930	15.5	4370	15,500
77	253	4.22	990	16.5	4220	16,500
78	244	4.07	1040	17.3	4070	17,300
79	235	3.92	1100	18.4	3920	18,400
80	224	3.74	1180	19.7	3740	19,700

FIG. 18. Sensible heat and moisture loss from human beings for 25 ft. per minute air motion.

Temp.	Total heat above 0° in one lb. air sat.	Cu. Ft. Per Lb.			Grains per lb. air sat.	Grains per cu. ft. air sat.	Temp.	Total heat above 0° in one lb. air sat.	Cu. Ft. Per Lb.			Grains per lb. air sat.	Grains per cu. ft. air sat.
		Sat. air	Dry air	Diff.					Sat. air	Dry air	Diff.		
0	.0	.....	.....	.....	.....	0.481	35	13.	12.54	12.46	.08	29.8	2.366
1	.35	.....	.....	.....	.....	0.505	36	13.5	12.575	12.485	.09	31.0	2.457
2	.70	.....	.....	.....	.....	0.529							
3	1.05	.....	.....	.....	.....	0.554	37	13.9	12.6	12.51	.09	32.2	2.550
							38	14.4	12.63	12.535	.095	33.7	2.646
4	1.4	.....	.....	.....	.....	0.582	39	14.9	12.66	12.565	.095	35.0	2.746
5	1.75	.....	.....	.....	.....	0.610							
6	2.1	.....	.....	.....	.....	0.639	40	15.3	12.685	12.585	.10	36.4	2.849
							41	15.8	12.72	12.615	.105	38.0	2.955
7	2.45	.....	.....	.....	.....	0.671	42	16.3	12.75	12.64	.11	39.4	3.064
8	2.8	.....	.....	.....	.....	0.704							
9	3.15	.....	.....	.....	.....	0.739	43	16.8	12.78	12.665	.115	41.0	3.177
							44	17.3	12.81	12.69	.12	42.7	3.294
10	3.5	.....	.....	.....	.....	0.776	45	17.75	12.845	12.72	.125	44.2	3.414
11	3.85	.....	.....	.....	.....	0.816							
12	4.2	.....	.....	.....	.....	0.856	46	18.25	12.875	12.745	.13	46.0	3.539
							47	18.75	12.90	12.765	.135	47.9	3.667
13	4.55	.....	.....	.....	.....	0.898	48	19.25	12.93	12.79	.14	49.7	3.800
14	4.9	.....	.....	.....	.....	0.941							
15	5.25	.....	.....	.....	.....	0.986	49	19.75	12.965	12.82	.145	51.5	3.936
							50	20.25	13.	12.85	.15	53.6	4.076
16	5.6	.....	.....	.....	.....	1.032	51	20.75	13.025	12.87	.155	55.6	4.222
17	5.95	.....	.....	.....	.....	1.080							
18	6.3	.....	.....	.....	.....	1.128	52	21.3	13.05	12.89	.16	57.8	4.372
							53	21.8	13.09	12.925	.165	60.0	4.526
19	6.65	.....	.....	.....	.....	1.181	54	22.4	13.125	12.95	.175	62.0	4.685
20	7.0	12.13	12.08	.04	15.0	1.235							
21	7.35	12.16	12.11	.05	15.9	1.294	55	23.	13.16	12.975	.185	64.4	4.849
							56	23.6	13.19	12.995	.195	66.9	5.016
22	7.75	12.18	12.13	.05	16.8	1.355	57	24.2	13.225	13.02	.205	69.2	5.191
23	8.2	12.22	12.16	.06	17.5	1.418							
24	8.6	12.24	12.18	.06	18.5	1.483	58	24.75	13.26	13.045	.215	71.7	5.370
							59	25.3	13.29	13.07	.22	74.5	5.55
25	9.0	12.27	12.21	.06	19.4	1.551	60	26.	13.325	13.1	.225	77.0	5.745
26	9.3	12.29	12.23	.06	20.4	1.623							
27	9.75	12.325	12.26	.065	21.2	1.697	61	26.6	13.365	13.125	.24	80.0	5.941
							62	27.3	13.4	13.15	.25	82.9	6.142
28	10.21	12.35	12.28	.07	22.1	1.773	63	28.1	13.44	13.175	.265	86.0	6.349
29	10.6	12.38	12.31	.07	23.3	1.853							
30	10.9	12.40	12.33	.07	24.2	1.935	64	28.75	13.475	13.20	.275	89.0	6.563
							65	29.5	13.51	13.225	.285	92.3	6.782
31	11.3	12.435	12.365	.07	25.2	2.022	66	30.25	13.54	13.250	.29	95.8	7.009
32	11.75	12.465	12.395	.07	26.2	2.113							
33	12.2	12.485	12.415	.07	27.4	2.194	67	31.0	13.575	13.275	.30	99.2	7.241
							68	31.8	13.615	13.3	.315	103.0	7.480
34	12.6	12.520	12.44	.08	28.5	2.279	69	32.6	13.65	13.325	.325	106.7	7.726

FIG. 19. Table showing thermal properties of air.

Temp.	Total heat above 0° in one lb. air sat.	Cu. Ft. Per Lb.			Grains per lb. air sat.	Grains per cu. ft. air sat.	Temp.	Total heat above 0° in one lb. air sat.	Cu. Ft. Per Lb.			Grains per lb. air sat.	Grains per cu. ft. air sat.
		Sat. air	Dry air	Diff.					Sat. air	Dry air	Diff.		
70	33.5	13.685	13.35	.335	110.2	7.980	105	77.6	15.385	14.235	1.150	355.0	22.750
71	34.3	13.725	13.375	.35	114.0	8.240	106	79.7	15.450	14.265	1.185	368.0	23.392
72	35.2	13.765	13.4	.365	118.0	8.508							
73	36.0	13.8	13.425	.375	122.0	8.782	107	81.8	15.515	14.285	1.230	380.0	24.048
							108	83.6	15.585	14.315	1.270	390.0	24.720
74	36.8	13.84	13.45	.39	126.4	9.066	109	85.5	15.645	14.335	1.310	405.0	25.408
75	37.75	13.88	13.475	.405	130.8	9.356							
76	38.7	13.92	13.50	.42	135.5	9.655	110	88.0	15.715	14.365	1.350	417.	26.112
							111	90.0	15.765	14.380	1.385	432.	26.750
77	39.65	13.96	13.525	.435	140.0	9.962	112	92.2	15.840	14.410	1.430	445.	27.310
78	40.5	14.005	13.56	.445	145.0	10.277							
79	41.5	14.04	13.575	.465	150.0	10.601	113	94.5	15.920	14.435	1.485	460.	27.880
							114	96.9	15.995	14.460	1.535	475.	28.600
80	42.5	14.085	13.61	.475	155.0	10.934	115	99.5	16.065	14.480	1.585	490.	29.600
81	43.5	14.125	13.63	.495	160.3	11.275							
82	44.5	14.175	13.66	.515	165.9	11.626	116	102.0	16.150	14.510	1.640	506.	30.100
							117	104.0	16.245	14.535	1.705	525.	31.000
83	45.6	14.205	13.675	.53	171.5	11.987	118	107.0	16.330	14.565	1.775	541.	32.000
84	46.65	14.26	13.71	.55	177.2	12.356							
85	47.75	14.30	13.725	.575	183.1	12.736	119	110.0	16.405	14.585	1.820	557.	33.300
							120	112.5	16.485	14.610	1.875	575.	34.80
86	49.0	14.35	13.76	.59	189.6	13.127	121	115.0	16.60	14.630	1.970	587.	35.40
87	50.2	14.40	13.78	.62	196.0	13.526							
88	51.35	14.45	13.80	.65	202.5	13.937	122	117.8	16.69	14.66	2.03	604.	36.20
							123	120.8	16.77	14.69	2.08	625.	37.30
89	52.7	14.495	13.825	.67	209.4	14.359	124	124.2	16.86	14.70	2.16	645.	38.20
90	54.0	14.545	13.86	.685	216.5	14.790							
91	55.25	14.585	13.88	.705	223.5	15.234	125	127.4	17.00	14.74	2.26	666.	39.20
							126	130.6	17.10	14.77	2.33	687.	40.10
92	56.65	14.635	13.91	.725	231.0	15.689	127	134.1	17.20	14.80	2.40	710.	41.20
93	58.0	14.685	13.93	.755	238.6	16.155							
94	59.35	14.74	13.96	.78	246.5	16.634	128	137.4	17.28	14.81	2.47	731.	42.40
							129	141.2	17.39	14.82	2.57	755.	43.50
95	60.9	14.80	13.975	.825	255.2	17.124	130	144.7	17.50	14.85	2.65	780.	44.60
96	62.6	14.855	14.015	.84	265.0	17.626							
97	64.1	14.905	14.03	.875	274.0	18.142	131	.....	.....	.....	.....	.....	.....
							132	.....	.....	.....	.....	.....	.....
98	65.6	14.960	14.06	.90	283.0	18.671	133	.....	.....	.....	.....	.....	.....
99	67.2	15.020	14.085	.935	291.0	19.212							
100	68.8	15.065	14.110	.965	303.0	19.766	134	.....	.....	.....	.....	.....	.....
							135	.....	.....	.....	.....	.....	.....
101	70.5	15.135	14.130	1.000	312.0	20.335	136	.....	.....	.....	.....	.....	.....
102	72.1	15.200	14.165	1.035	322.0	20.917							
103	74.0	15.260	14.185	1.075	333.0	21.514	137	.....	.....	.....	.....	.....	.....
							138	.....	.....	.....	.....	.....	.....
104	75.7	15.325	14.215	1.110	344.0	22.125	139	.....	.....	.....	.....	.....	.....

FIG. 19. Table showing thermal properties of air.

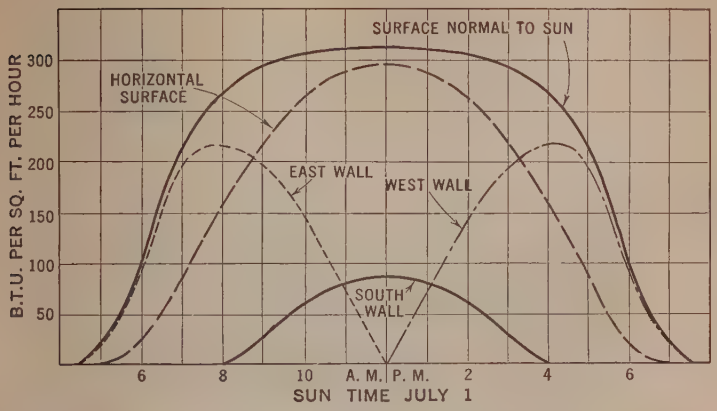

FIG. 20.[38] Curves giving solar intensity normal to sun, on horizontal surface and on walls for July 1, Latitude 40° N.

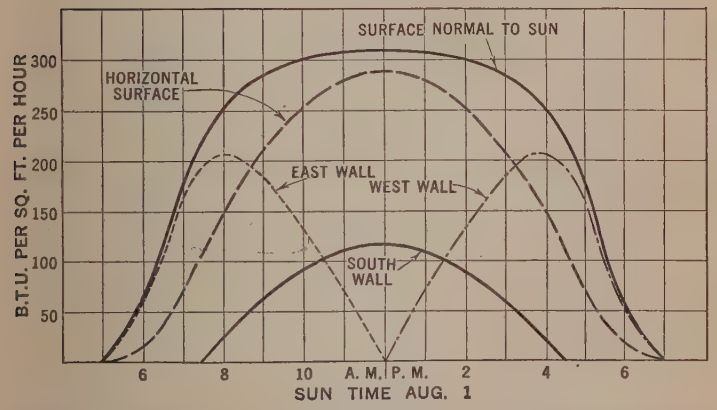

FIG. 21.[38] Curves giving solar intensity normal to sun, on horizontal surface and on walls for August 1, Latitude 40° N.

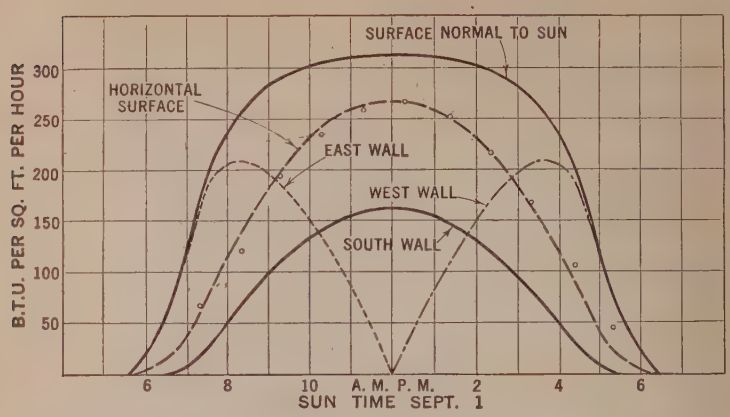

FIG. 22.[38] Curves giving solar intensity normal to sun, on horizontal surface and on walls for September 1. Points give Weather Bureau data for horizontal surface. Latitude 40° N.

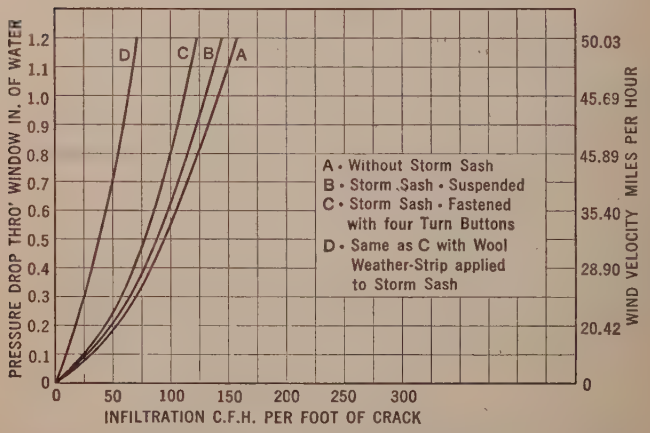

FIG. 24.[52] Infiltration through sash perimeter of window with and without storm sash—5/64 in. crack and 1/32 in. clearance.

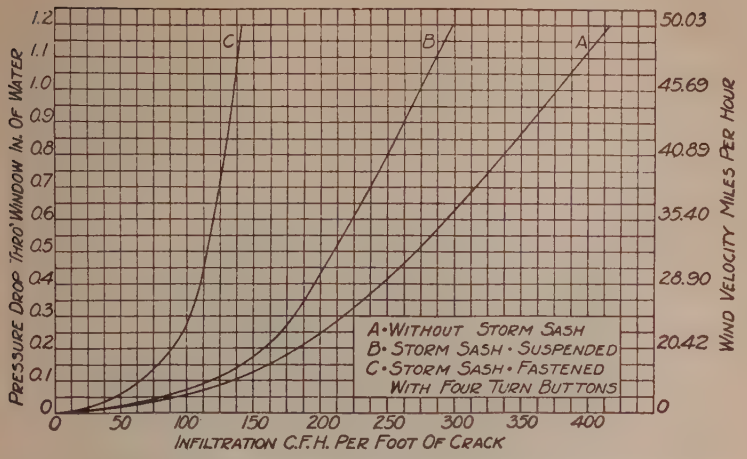

FIG. 25.[52] Infiltration through sash perimeter of window with and without storm sash—⅛ in. crack and ⅛ in. clearance.

FIG. 26. Typical ejector type heating and air conditioning unit for multi-story buildings. Air supply from central plant, as shown in Fig. 27.

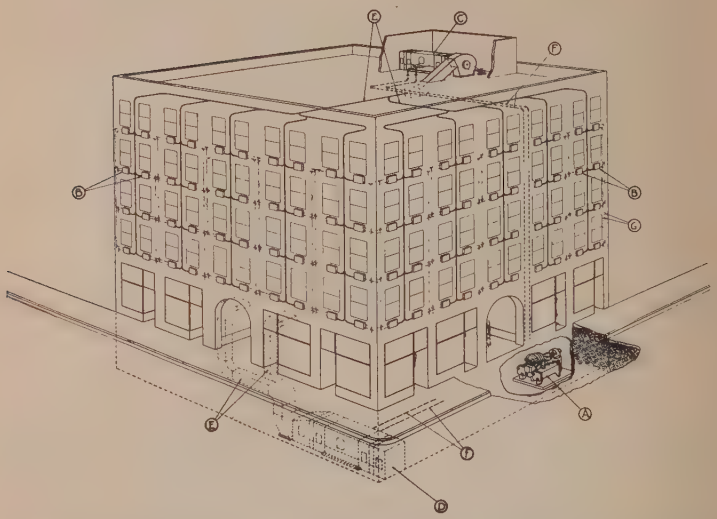

FIG. 27. Schematic drawing showing typical air conditioning system for a multi-story building. Central refrigeration plant in basement. Air conditioning apparatus consisting of fan, filters and dehumidifiers on upper floor. Ejector type re-circulating cooling unit with winter heating coils under each window, as shown in Fig. 26.

A—Refrigerating Machine.
B—Weathermaster Units.
C—Air conditioning apparatus for offices on upper floors.
D—Air conditioning apparatus for stores.
E—Air ducts.
F—Cold water piping.
G—Steam and return piping.

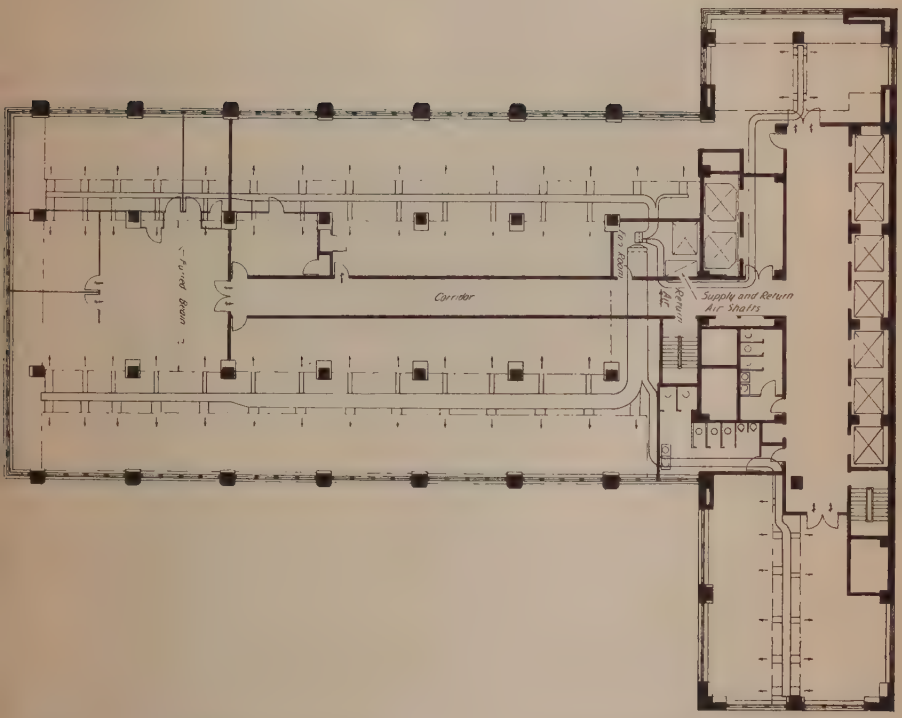

FIG. 28. Arrangement of air conditioning ducts on typical floor in multi-story office building.

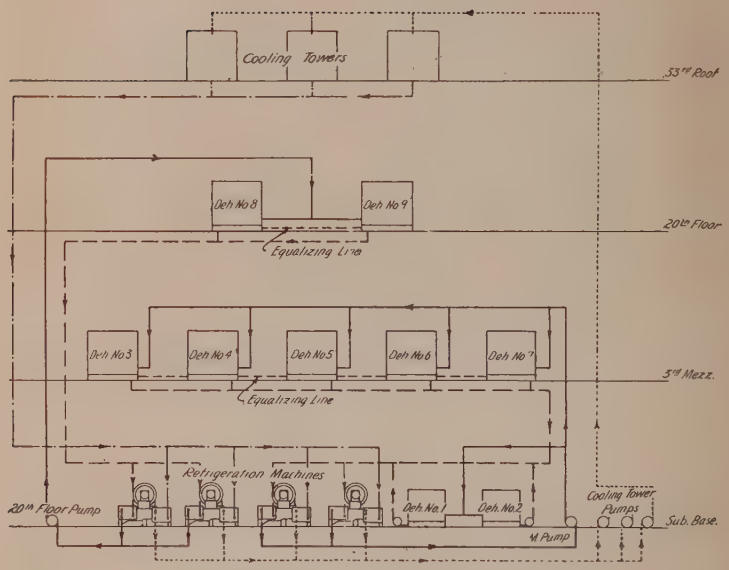

FIG. 29. Diagrammatic scheme showing location of equipment and re-circulation of water in air conditioning system for multi-story office building.

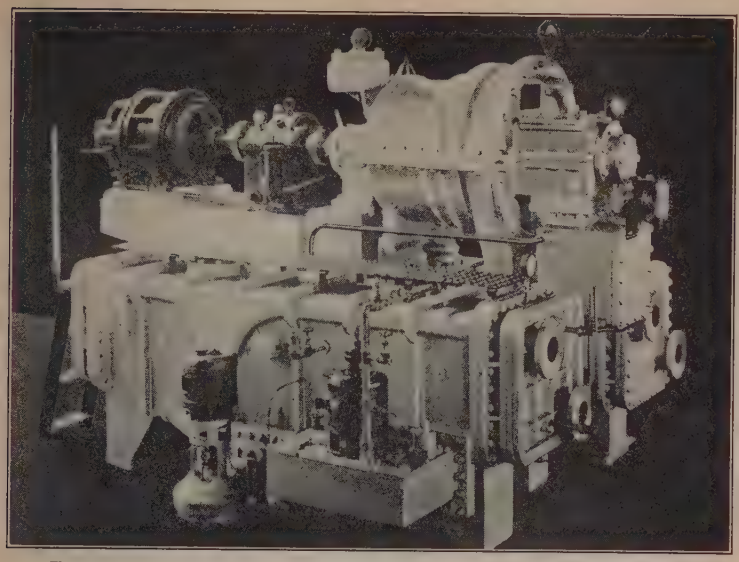

FIG. 30. Centrifugal Refrigeration Machine using dichloromethane as refrigerant.

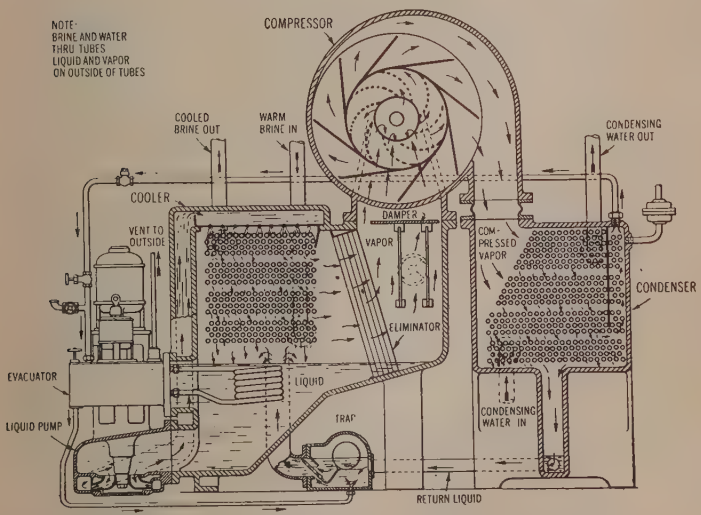

FIG. 31. Typical diagram of Centrifugal Refrigeration Machine.

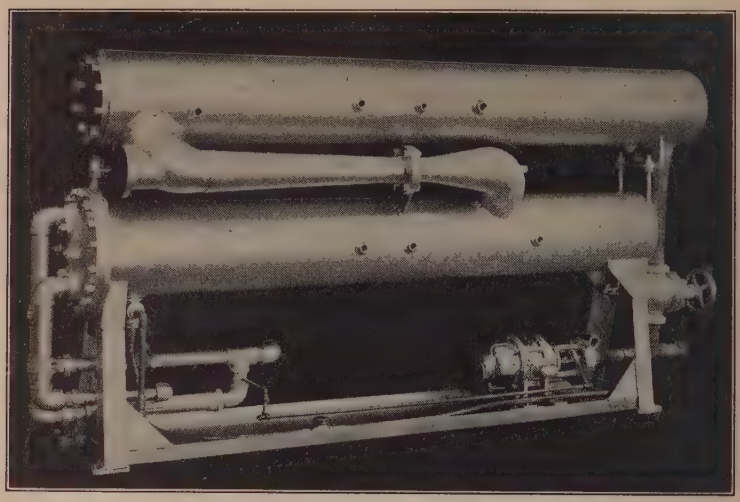

FIG. 32. Steam Ejector Refrigeration Machine.

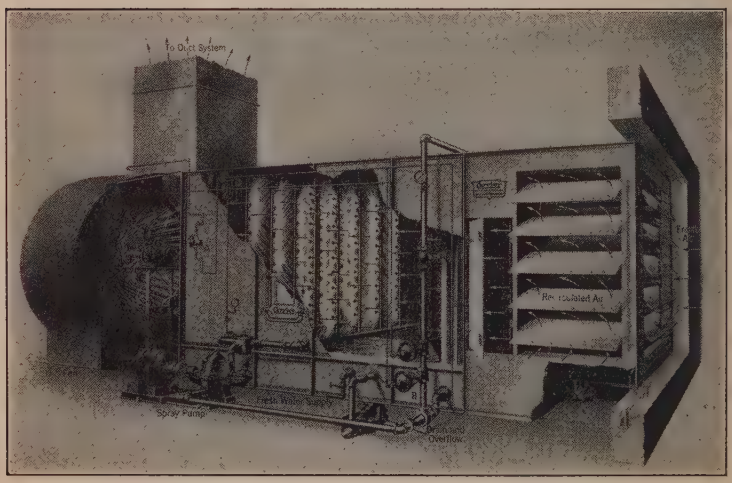

FIG. 33. Typical air conditioning apparatus showing fan, dehumidifier, water pump, return and outside air damper.

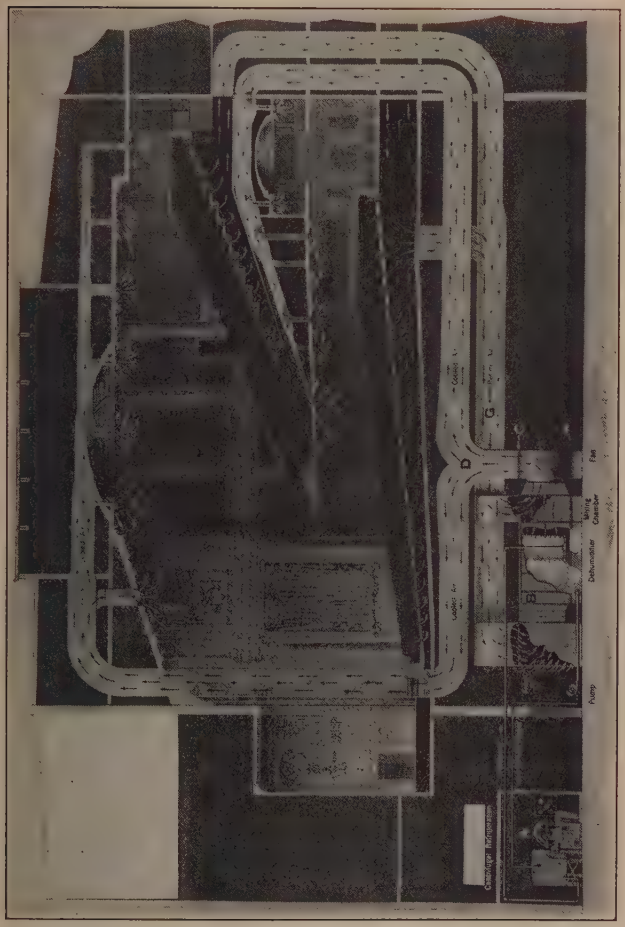

FIG. 34. Typical theatre air conditioning installation showing refrigeration, dehumidifier and fan with by-pass, and downward method of distribution through pan outlets.

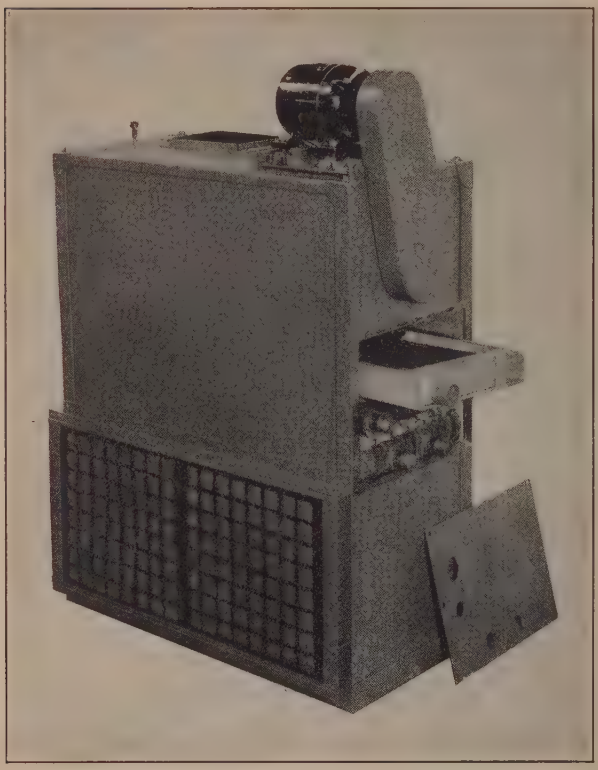

FIG. 35. Typical vertical air conditioning unit consisting of fan, filters and cooling coil.

FIG. 36. Typical installation of air conditioning unit above the bulk window of a retail store. This unit will take care of an average store 30 ft. wide, 75 ft. deep. Refrigeration located in basement.

FIG. 37. Unit type air conditioning unit, complete with fan, filter, target type humidifier, cooling coils and heater. Refrigeration obtained either by the circulation of cold water from central plant or by direct expansion from a small refrigerating unit.

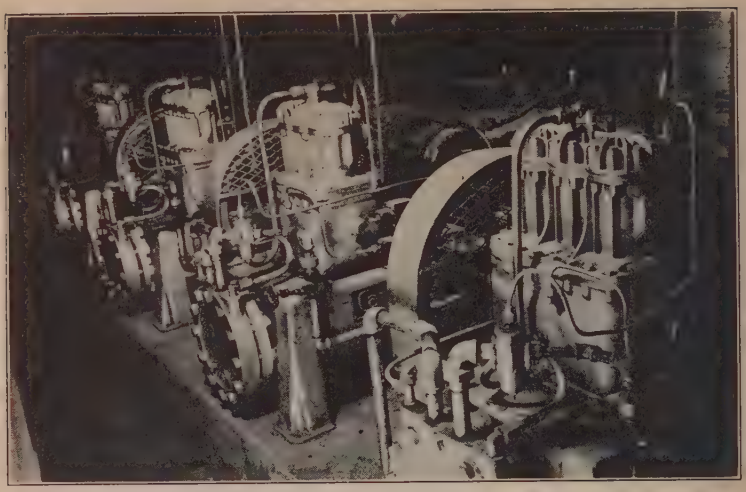

FIG. 38. Battery of Freon refrigeration machines in basement of retail store.

FIG. 39. Self-contained air conditioning unit, containing fan, filter, cooling coils and refrigerating unit.

Discussion

Chairman Dorr: Mr. Davidson's paper is open for discussion Any questions to be asked Mr. Davidson?

Leroy A. Smith (Viscose Co.): I should like to ask what would be the approximate cost of that humidifying unit as put into a home to be connected, perhaps, to a hot water heater.

P. L. Davidson: The small one illustrated in the paper would cost approximately $250.00 installed.

Chairman Dorr: Is that heating as well?

P. L. Davidson: No, that must be used with your present heating system to humidify the heated air.

E. G. Walker: Can you give any unit cost to build an industrial air conditioning plant? Say, the unit cost per thousand cubic feet?

P. L. Davidson: Yes, we have worked that out. I haven't those figures and cannot give them off-hand.

C. L. A. Wynd: What would be the best way to maintain a controlled load, say around ten per cent—very low humidity?

P. L. Davidson: On a year around load of ten per cent, perhaps the best thing to use would be silica gel. That's an absorption proposition, developed by the Davison Chemical Company, and when you attempt to maintain ten per cent, at ordinary room temperatures, you are getting below not the theoretical limit but the economical limit of mechanical refrigeration.

D. R. Kellogg: I rise to ask a question prompted by your statement that silica gel is the material to use. Now, I am not a Company man. We have used activated aluminum in our plant very successfully. Have you any experience as to the relative merits of the two?

P. L. Davidson: No, I have not.

D. R. Kellogg: We have used it, not for air conditioning, but for getting air with a dew point of minus 50 and 60 and for that purpose it has been ideal. We have also used silica gel but the activated aluminum we have found very much cheaper.

R. J. Thompson: There are three points I would like to bring out. One is that the statement is made that "This centrifugal machine is compact and occupies less than one-quarter of the space required by a reciprocating machine." That statement might be considered debatable as with some of these large machines, of various types—and I make no attempt to favor any particular one, it is simply a question of getting capacity out of a given amount of space because we know of installations using various types of machines, all of them perfectly satisfactory, which occupy, substantially the same amount of floor space.

Now, the second point refers more directly to the refrigerant Freon, or F-12. It is mentioned as being "practically harmless at room temperatures." Well, we might ask, "What is meant by 'practically harmless'?" And I would venture to point out the fact that it is harmless under all conditions of toxicity, inflammability and explosiveness, as confirmed by the Underwriters Laboratory, U. S. Bureau of Mines, R. I. 3013 and 3042.

And the third point is the statement made that this particular refrigerant will probably replace certain elements, except in the largest sizes. By that I suppose is meant depending upon the nature of the refrigeration machine. One of the installations now using Freon and, probably, one of the larger capacity installations, is up to 1980 tons, three compressors of 660 tons each, and that, I believe, would qualify the point raised, that this particular refrigerant is quite adaptable in the larger types of machines.

P. L. DAVIDSON: Those of course are debatable points. The question of whether you use Freon or Zeron or dichloro-methane is a matter of personal opinion. I take the view that its adaptability to centrifugal refrigeration makes it more desirable. Other people might have other opinions.

Now, so far as space requirements go, for a reciprocating machine, if you hang your condensers on the ceiling and put only your larger equipment on the floor, your actual floor space may not be that much greater, but in a great many installations—in that actual installation used in the paper for instance, the centrifugal type uses one-quarter of the space of that required for reciprocating machine.

J. R. WITHROW: The conclusions of the paper, especially from the various physiological aspects, were very interesting and, without doubt, correct. However, one cannot help mentioning the thought that runs through one's mind of what is the matter with the Pullman car when he enters it. It isn't always just the varying temperatures; there seems to be something else. I remember one time Harry W. Wiley, the food administrator, made a speech in Omaha in which he said the Pullman Company had just contributed the eighth wonder of the world by delivering a car of air from Chicago to Omaha without losing a litre.

Referring to the same point in the paper, I think that it is not enough to make an experiment where the patients are sitting outside the room and breathing material through the tubes because we all know when we come into a committee room, for instance, filled with tobacco smoke, that we can immediately feel a sensation on the skin. Maybe it is humidity but I suspect it is toxic effect and for a long time I have wondered why the physiological chemists do not put their

patient in a rubber suit, but that, of course, again changes the humidity conditions. I am not saying the conclusions are not entirely justified but the sealed tube is certainly not the answer.

P. L. DAVIDSON: This is only one of many experiments which have been made, but we who are in the industry feel quite certain that the sensation of air conditions designated as "stuffiness," is undoubtedly due to the fact that the thermal properties of the air in the room upsets your normal equilibrium, that is, your heat balance. In other words, you must change your normal function; you may have been losing heat by radiation and conduction, and when air conditions change then the only way you can dissipate that heat is by perspiring—evaporation and perspiration, and any change in that equilibrium will affect you.

Now there is something else in air conditioning—ionization. Three or four years ago ozone was advanced as the solution that ozone would put something in the air that would make any air conditioned room feel like the country on a bright May day. Ozone has been tried and the cure was worse than the disease. To get enough ozone in to do any good, the effect of the ozone itself was obnoxious. Now we have come to ionization. Ionization of air seems to have quite a beneficial effect; there is something there, something intangible, which makes ionized air a little better than the un-ionized, but any room in which people are staying, indoors, regardless of whether it is ventilated or not, if the air is ionized when the room is vacant, as soon as two or three people go in it is immediately neutralized, so that the lack of ionization is not caused by air conditioning or ventilation, it is lacking in any occupied room.

CHAIRMAN DORR: Gentlemen, the time is up for our technical session. We thank the authors for their papers.

A PRINTING INK AND METHOD FOR DISCHARGING FROM PAPER

By SIDNEY D. WELLS*

The increasing demand for paper making fiber has frequently directed the attention of paper makers to printed paper as a source of supply. Numerous processes for the liberation and removal of the carbon black pigment are known and some paper making plants have for a long time secured a large portion of their fibrous raw materials from paper stock recovered from discarded books, periodicals, and other publications printed on paper composed of cellulose fibers free from lignin (the principal non-cellulose constituent of wood fibers which have not been chemically purified).

There is a large quantity of paper of this character available but a much larger tonnage of printed paper contains groundwood pulp, the fibers of which pulp have not been chemically purified to remove the lignin constituent of the ligno-cellulose. Practically all of our newspapers and other publications, such as telephone directories, catalogs, agricultural publications, advertising circulars, etc., use paper of this sort. Papers containing groundwood pulp are desirable, on account of their excellent printing qualities and opacity as compared with the higher priced chemical pulp papers, for use where the permanency of record is not of importance but accurate presentation of the message is necessary and the weight and bulk of the publication is important as a matter of convenience or in the cost of distribution.

Numerous attempts have been made to remove the ink from printed groundwood papers but the recovered pulp fiber has not been sufficiently bright in color to permit its substitution for virgin stock. The difficulty encountered in the removal of printing ink from groundwood papers is caused by:

1. Detergents depending upon slight alkalinity to disperse the vehicle and varnish of printing inks have discolored the ligno-cellulose fibers or at least reduced the brightness of their color to a point

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below which they cannot be used in making paper which meets the standard requirements of brightness.

2. Bleaching agents such as calcium hypochlorite when used to bleach any discoloration, have been unsatisfactory because of the great demand of lignin for chlorine producing lignin chloride which is deep brown in color.

3. The groundwood fibers contain such a large proportion of fine fibrous debris that the particles of carbon black used for the pigment of the ink are closely immeshed and can only be washed out by the copious use of water which invariably causes the loss of prohibitive amounts of fiber.

In view of the difficulties that have been encountered in the attempt to remove the chemically inert carbon black pigment universally used for black printing ink, numerous attempts have been made to develop an ink based upon a pigment that can be bleached or discharged and removed from the fiber by solution. A search made in 1928 revealed attempts to substitute for carbon pigment black lakes of various dyestuffs or mineral pigments capable of resolution into colorless and soluble compounds. Such search showed that successful solution of the problem required the production of an ink which would compare favorably with carbon ink in printing halftones, covering power (mileage), color and wear on printing plates.

Before starting on the development of a dischargeable printing ink it was necessary to investigate the possibilities for using such ink in the field of publication that used a sufficient tonnage of paper to furnish an adequate supply of printed paper and which printed paper could be readily collected and assembled at a central point. The most ideal publication for the purpose proved to be telephone directories. Telephone Companies in the larger cities issue new directories semi-annually and practically all Telephone Companies, when issuing a new edition, make special efforts to collect all of the obsolete directories in order to avoid the loss of time and expense which is occasioned at central telephone exchanges when the public uses obsolete directories. The proportion of obsolete directories recovered by the Telephone Companies is very high and since such collection is in responsible hands, long time contracts could be made for such raw material.

With the assurance that the supply of recovered telephone directories could be contracted for and that the proportion of directories

printed with special ink which would be lost to the recovery process would be relatively small the problem of developing a suitable ink was placed in the hands of printing ink specialists. After an experimental period there was produced in the laboratory of the Hilton Davis Company of Cincinnati, Ohio, a pigment composed of the iron lake of haematein which was compounded into a printing ink that met all the requirements of the printer and publisher and which was capable of being either bleached with hypochlorite solutions or discharged with reducing agents such as sulphur dioxide in the presence of moisture and the discharged product dissolved in dilute sulphurous acid. The development of this ink depended upon knowledge of the principles involved, the problems of the printer and long experience in and contact with the manufacture of printing inks and printing. While the cost of the ink in the development stage is more than that of the inks based upon carbon black which were used previously, the increase can be absorbed in the margin between the cost of the recovered stock and virgin stock.

As soon as it was apparent that a satisfactory ink was available the problem of developing a satisfactory paper recovery process was undertaken, first in the laboratory, then on a pilot plant scale and finally in a plant having a productive capacity of over sixty tons of recovered stock per day.

The use of calcium hypochlorite as a bleaching agent was recognized as a possibility for the recovery of the paper stock but the difficulty of using it on a stock containing groundwood seemed to make it undesirable from the standpoint of technical control and also because the quantities of reagent necessary indicated a manufacturing cost greater than considered permissible. It soon became evident that working with sulphur dioxide as a reducing agent would yield the most economical process available.

The first efforts to recover the paper stock printed with the new ink followed the common practice of working with pulp suspensions of about three per cent consistency. Treatment of such suspensions with sulphur dioxide gas sufficient to create a concentration of five grams per liter resulted in the discharge of the ink in about twelve hours. Increasing the concentration to ten grams per liter reduced the time to about three hours. Use of solutions of this strength or greater would be extremely difficult and disagreeable in beaters, Belmer bleachers or similar open types of pulp mixing and circulating equipment and the washing of the pulp on rotary filters of standard

construction would also create unbearable conditions for the operators. Actual mill trials confirmed these observations and made it necessary to investigate the possibility of treatment in closed vessels.

A barrel type butter churn was next used with a hollow trunnion through which sulphur dioxide gas could be admitted as desired while revolving. Macerated printed paper stock at a consistency of twenty per cent was charged until the churn was filled two-thirds full. Gas was admitted until a concentration of fifty grams per liter was attained. This concentration required twenty pounds of gas per hundred pounds of paper stock dry weight. Under these conditions the ink was discharged in twenty minutes. After discharging water was added to bring the stock consistency to about ten per cent and the mass pressed to a consistency of twenty-five per cent in a wine press. It was then mixed with water to a consistency of ten per cent and pressed again. A repetition of this step produced a bright pulp entirely satisfactory for use in the manufacture of white papers. It was then found that the liquors removed from one batch were capable of removing ink from untreated stock. Diffusion washing seemed desirable if possible and studies along this line were next undertaken in a trial diffuser five inches in diameter and thirteen feet high.

The diffusion studies soon made manifest that paper stock composed of groundwood and sulphite was entirely too impervious to water to permit a satisfactory rate of diffusion through a reasonable height of stock. The usual furnish as it passes onto a paper machine will have a freeness of between 115 and 135 as measured by the standard Canadian freeness tester. Sulphate pulps which are commonly washed by diffusion will show freeness tests from 600 to 700. The problem was to put a stock having a freeness below 135 into such form that it acted like a stock having a freeness above 600.

Earlier work with the rod mill indicated that when pulp is passed through such a rod mill with about four parts of water to one part of dry fiber the stock leaving the outlet is in the form of little pellets or nodules, highly absorbent and of uniform density throughout. The use of the 3'x5' rod mill at the Forest Products Laboratory was then secured and batches of printed telephone signatures treated. Very satisfactory nodulization occurred and the consistency of twenty per cent was found to be best for the purpose. Freeness tests on nodulized telephone directory paper ran between 600 and 750.

The nodules obtained in these runs were then treated in the dif-

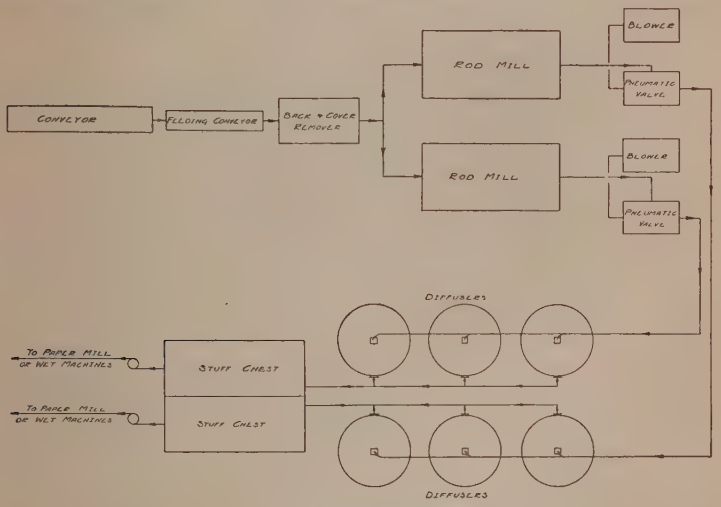
fuser and it was found that satisfactory washing was possible, that countercurrent washing was satisfactory and economical and that the nodules could be treated with sulphur dioxide in the diffuser before the diffusion was commenced. It was also found that more rapid diffusion and less packing took place by passing the liquors from the bottom up through the stock rather than from the top down as is more usually done when washing sulphate pulp.

The next step was to prove the feasibility of the diffusion principle on a larger scale and a pilot diffuser three feet square and with a height between perforated false top and bottom of thirteen feet was provided. Several tons of printed paper were nodulized in one of the 7'x16' rod mills at the Nekoosa Edwards Paper Company, Nekoosa, Wisconsin, and the nodulized stock shipped to Combined Locks, Wisconsin, in a refrigerator car so as to maintain constant and uniform moisture. Several one ton batches were treated in the diffuser and the stock free from ink was run into white printing paper on a commercial paper machine. The paper obtained was printed on a commercial press then using the new ink and thus the cycle was completed. The pilot operation indicated a sulphur dioxide consumption of sixty pounds per ton of stock and that no step in the cycle presented serious difficulties. On the basis of these tests our Engineering Department designed a plant capable of producing over sixty tons of recovered stock per day and the plant was constructed in the summer of 1932.

The progress of the paper stock during the process is shown in the accompanying flow sheet. The flow is divided into two lines after leaving the back and cover remover in order to separately handle white and colored paper. The white paper is passed through one line and the colored paper through the other. After removal of the ink the stock recovered from the colored paper is used in the manufacture of colored papers. The books come from various cities in bundles of the same size and are stored in piles.

The back and cover remover is an adjustable machine that will satisfactorily handle books of various size. The books are introduced into the feeding conveyor and are thereby delivered to the back and cover remover which cuts off about three-eights of an inch of back, removes the covers and separates the leaves according to color. Each color of leaves is conveyed to a 5'x14' Marcy rod mill and the necessary water is added to produce nodules of between twenty and twenty-five per cent consistency. Each mill will nodulize

two tons of dry paper per hour with the expenditure of ninety horsepower. The nodulized stock drops into screw conveyors which deliver it to a Voith pneumatic conveying system which blows it through pipes three inches in diameter to the diffusers located in a building about sixty feet away. There are six diffusers which consist of wooden stave tanks fourteen feet in diameter and twenty feet high provided with false bottoms and tops made of perforated sheet metal about eight inches from the wooden top and bottom of each tank.



Flow Sheet for Paper Stock.

The false bottom is chromium nickel steel alloy such as is used for sulphite blow pits and the false tops of closely perforated sheet bronze, No. 65, such as is used for centrifugal screens. The tops thus permit of the maximum discharge of diffusion liquor while the bottoms are of sufficient strength to support the weight and at the same time permit the distribution of the gas, diffusion liquors and wash water. The diffusers are in two lines of three each and rest upon concrete chests wood lined, shaped like Belmer bleachers and provided with circulating pumps. Each diffuser and each chest hold approximately fifteen tons of stock at different consistencies. On dumping from a diffuser to the chest below sufficient water is used to reduce the consistency to between four and five per cent. From the chests the stock is pumped to rotary filters where all trace

of acids is removed and from there the stock is either delivered to the paper mill or run into laps for storage.

While a diffuser is being filled with nodules gas from a rotary sulphur burner is blown into the bottom and is absorbed by the moisture in the nodules. Maintenance of the strength of diffusion liquors calls for the burning of 400 # of sulphur to each diffuser charge of about 15 tons of paper stock. On filling and closing each diffuser the gas connections are shut and strong liquor from earlier diffusions is pumped into the bottom until the diffuser is filled and the liquor passes out through the connections at the top to the weak liquor tank, strong liquor tank, or sewer depending on the sulphur dioxide content. The cycle for each diffuser takes twenty-seven hours. The distribution if the liquor to and from each diffuser takes place as follows:

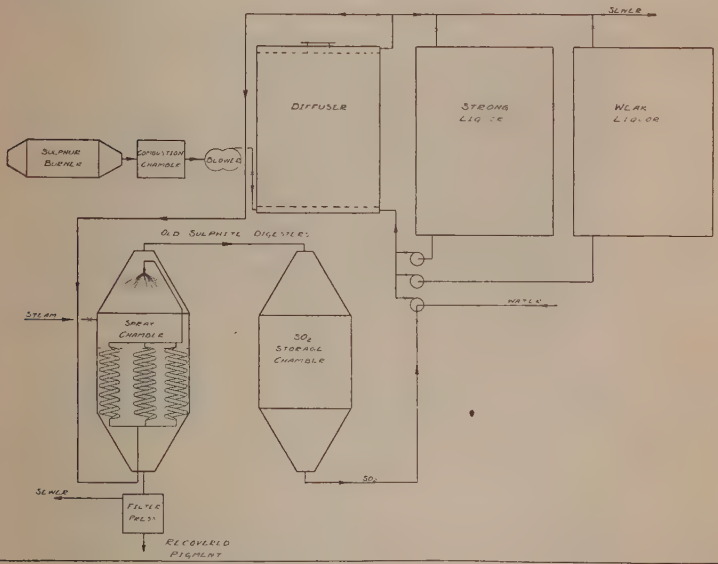
To Diffuser	From Diffuser
3 hours on strong liquor	3 hours filling with liquor
3 hours on weak liquor	1 hour to weak tank
21 hours on water	3 hours to strong tank
	2 hours to weak tank
	18 hours to sewer

The average test of liquor to the strong tank is 6 grams per liter of SO_2 and to the weak tank 4 grams per liter of SO_2. Liquors testing below 2 grams per liter of SO_2 are discharged to the sewer.

While the plant is designed for a production of over sixty tons per day the decreased demands for stock during the past year have made it possible to leave the diffusers washing with water longer than is shown in the schedule. The rate of flow through each diffuser is sixty gallons per minute. Recent tests show that the addition of sulphur dioxide to the water, during the first six hours a diffuser is on water, improves the operation.

Experiments show that the boiling off of sulphur dioxide from strong liquor leaving a diffuser will furnish a supply of sulphur dioxide undiluted with nitrogen. Two small abandoned sulphite digesters were made available and are being connected up to provide the recovery system shown in the accompanying flow sheet. The upper portion of one digester will act as a spray chamber for driving off the sulphur dioxide by means of steam while the lower portion will be provided with coils immersed in the descending liquor to absorb

much of the heat contained therein by heating the incoming liquor passing through the coils on its way to the spray nozzle. The other digester will serve as a storage tank for sulphur dioxide so as to permit continuous operation and intermittent supply of gas. The pigment contained in the liquor is precipitated by release of the sulphur dioxide and by neutralization of any residual acidity with caustic soda.



Flow Sheet for Liquor Use and Recovery.

With the operation of the recovery system the distribution to and from each diffuser will be as follows:

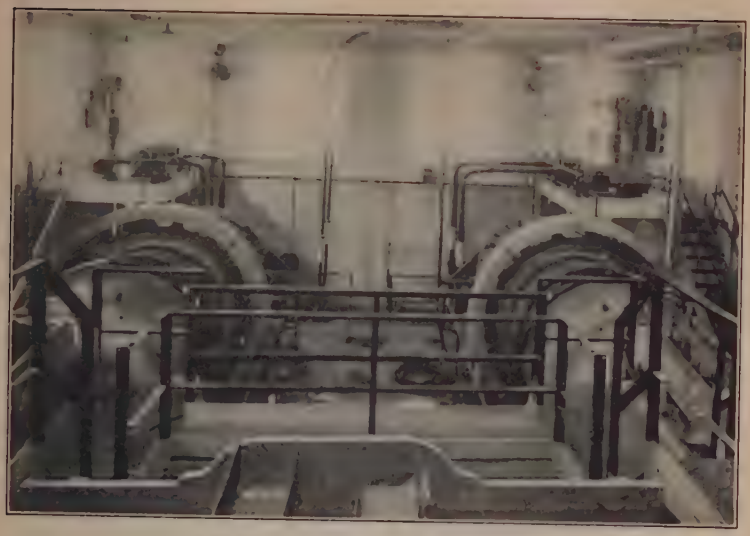
To Diffuser	From Diffuser
3 hours on strong liquor	3 hours filling
3 hours on weak liquor	1 hour to weak tank
6 hours on sulphited water	6 hours to recovery
15 hours on water	3 hours to strong tank
	2 hours to weak tank
	9 hours to sewer

While the liquors will be of approximately the same concentration in sulphur dioxide as at present they will contain less pigment

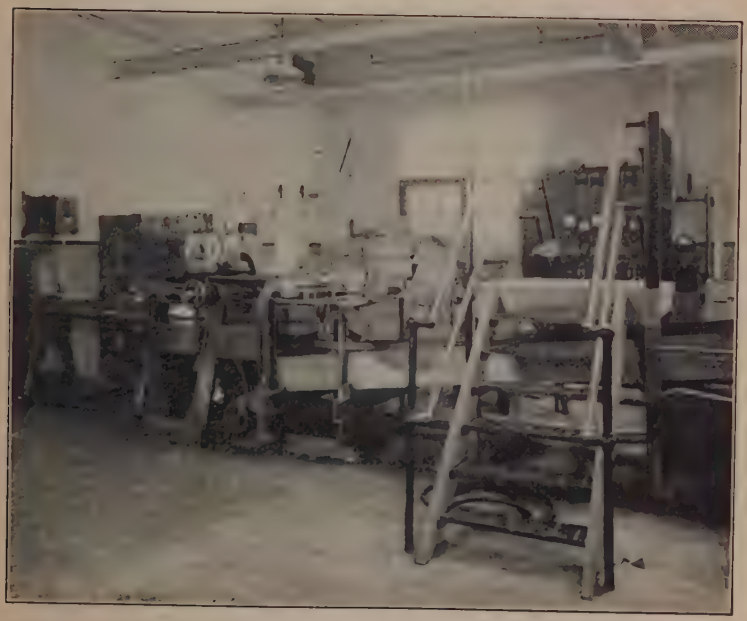
in solution and remove the possibility of any slight discoloration of the pulp.

The use of dischargeable printing ink based upon a pigment consisting of the iron lake of haematein has now been continuous throughout a period of two years. The recovery of the groundwood paper printed with this ink has been taking place in large quantities throughout the past year. Telephone books in the larger cities in the territory from Omaha to New York City and north of the Ohio River are now printed with this ink and the recovered directories are shipped to the Combined Locks Paper Company. In the manufacture of white printing paper higher in quality than telephone directory paper, it is satisfactory to use large percentages of stock recovered from this process, in fact in some grades of printing paper as high as 80 per cent of such recovered stock can be used to replace a like quantity of virgin pulp. In consequence a new paper making material has been made available, which forms an important item in our national inventory of fibrous stock and the supply of such new material can be greatly increased should it become important to further increase our national inventory of paper making stocks.

The development described above called for patience and vision during a period when business depression demanded curtailment in research and development work.



Rod Mills and Pneumatic Conveyors.



Back and Cover Remover

Discussion

Chairman Dorr: Gentlemen, the paper is open for discussion.

H. J. Skinner: I should like to ask Mr. Wells if it is necessary to use a rod mill or whether any other type of pulp disintegrating apparatus would work equally well?

S. D. Wells: I think the Lannoye Pulper or any pulper equipment capable of working up stock to say twenty or twenty-five per cent consistency would be satisfactory. A rod mill takes only ninety horse power, however, and you get a production of two tons an hour. I do not think there is any other type of equipment that can give anywhere near that and produce the stock in such form that by dropping it with more water into an ordinary Belmer Bleacher, it will produce the completely disintegrated slush pulp of usual type which we use in the paper mills.

H. J. Skinner: Would you not get an additional beating action in the rod mill?

S. D. Wells: At that consistency there is very little. Of course at that tonnage there is a certain amount of hydration, but there seems to be much less than if we ran it at, say six per cent, which is the more usual consistency in handling stock in a paper mill.

H. W. Elley: Apparently the success of this process will depend on having stock free from carbon black printing inks. I wonder whether it would be feasible to collect stock from different sources other than telephone directories and still run this process without having complications of having some carbon black material in it.

S. D. Wells: It is necessary to keep the carbon black ink out. That presents one difficulty in extending the use of this ink to newspapers. For instance, until a very large proportion of newspapers use it, the papers would have to go through a sorting department in the paper mill which, of course, now takes place in the usual paper recovery operation, where we use free ground wood sheets such as the Saturday Evening Post. The girls have to pick out any ground wood sheets in that operation, which they do very effectively. Of course, that adds a couple of dollars a ton to the cost of the paper, but that could be worked out if there was enough margin to make it worth while to do so.

H. W. Elley: Does the use of this special ink add a great deal to the cost of the recovered stock.

S. D. Wells: It does not. It is my impression that the added cost is approximately $2.00 per ton of paper. In their arrangement with the Telephone Company the Combined Locks Paper Company absorbs that cost, which is a well worthwhile arrangement on account of the form in which the books come to them and the way they work up in their operation.

V. L. King: Is there any injury to the fiber, softening of the fiber, that you would experience on continued re-use of the pulp?

S. D. WELLS: So far as the re-use of the paper is concerned, if we were dependent one hundred per cent on this paper, and if the Telephone Companies used only our paper there might be some difficulty. I do not know whether there would be or not. As a matter of fact, though, the telephone companies get their paper from many other sources than from our mill which, of course, always use virgin stock. In our mill we have water power grinders and it is necessary for us to use that water power to the extent which we have it in grinding wood, we have no better use at the present time for it, so that the paper in our average operation may contain as high as fifty per cent of this recovered stock. But in the paper coming back, I imagine a very small part of it has been used more than once.

V. L. KING: I should also like to ask whether there are any other printing inks with which you have had experience that are susceptible to re-use and removable, either with sulphur dioxide or with other chemicals?

S. D. WELLS: Yes, we have had papers printed with other inks submitted to us for de-inking, that is on a small scale, not on mill scale but in the laboratory. There are a number of pigments capable of discharge which may be made from lakes of various organic dyestuffs. I am not familiar with the dye industry so that I cannot go into that very intelligently, but I know there are natural blacks, and some sulphur blacks that are capable of discharging. It is purely an economic question with us, as to the cost of the pigment, and I think this logwood black is one of the lowest priced blacks, in proportion to its covering power and other properties, that is available.

V. L. KING: What I thought you might say was that there were other blacks that could be removed without the necessity of using such material as sulphur dioxide, which requires you to use the equipment which you described.

S. D. WELLS: It is awkward to use sulphur dioxide, but it is about the cheapest chemical you could imagine. Four hundred pounds of sulphur, in the form of sulphur dioxide, is sufficient to maintain our liquors at the desired strength for treatment of fifteen tons of paper so that as de-inking costs go, that is a ridiculously low cost—and our diffusers are wooden tanks.

J. W. LIVINGSTON: Is there any literature on this process of re-use, that is, taking telephone books, discharging the ink and printing them again. How long can this process go on?

S. D. WELLS: The re-use of the fiber, you mean?

J. W. LIVINGSTON: Yes.

S. D. WELLS: Up to the present time we do not know. We have run into no difficulties from the re-use of this fiber, but we do not get back more than twenty-five per cent of the stock that we need in our operation. How soon we would get into trouble if we got back eighty per cent I do not know. However, it is not likely that any mill would get back eighty per cent of paper which they had made, because most

of the customers buy their paper from various sources, so that there is going to be the freshening of the stock with other virgin stock sufficient to prevent any trouble from that source. In the City of Kalamazoo the paper industry is almost entirely dependent on recovered magazine stock.

J. W. LIVINGSTON: The whole subject sounds fascinating from the point of view of those who have felt concerned about the exhaustion of our forest resources used to a large extent for newspaper stock. With our process there is a possibility that the raw stock used can be cut down to one-half or even less.

S. D. WELLS: It could if the collection problem were solved. In the case of telephone directories we have a source where the collection problem has been worked out up to approximately eighty per cent. From a study of available statistics I believe that twenty-five per cent recovery of newspapers would be a very high figure. I do not think we average anywhere near that at the present time.

J. R. WITHROW: I should like to inquire about the permanency of the ink?

S. D. WELLS: I was not in touch with the tests made, but I understand the Western Electric Company, who supervises the printing of all the telephone books, has made very thorough tests of the ink and are satisfied from the standpoint of permanency. Personally, I believe the ink is much more permanent than the paper on which the ink is used.

A. E. MARSHALL: With reference to Dr. King's question on inks, I should like to know whether there is a sufficient supply of logwood, supposing the process extends, to take care of the ink requirements on a logwood basis, or whether other inks would not have to come into the picture.

S. D. WELLS: I would like to ask Mr. Drew to answer that question.

MR. DREW (American Dyewood Company): At the rate logwood consumption is falling off, due to being supplanted in textile industry with other dyes, I believe if all the newspapers in the country were printed with logwood ink, it would not consume the output of one company. This is my best estimate.

H. J. SKINNER: Can you use this ink exactly the same as the others?

S. D. WELLS: Yes, it is my understanding they have made no modification in regard to that point on the presses. The ink is in an oil vehicle just the same as the carbon black ink.

E. L. WILSON: Do you have to pay a premium to the printer for the purchase of his waste stock, or to the telephone company? That is, when you get the books back, do you pay more for the books as waste paper than if they were sold on the regular market?

S. D. WELLS: We pay a slight premium. Of course we always

have to furnish the printer with ink at the price of carbon black ink, which costs us a little more, so that amounts to a certain premium.

E. L. WILSON: I was not thinking of that as a premium. Of course, on that basis, the printer is paying the same for his ink because you are bearing the extra cost. My question was whether, when they sold you the books, they received more than they would receive for them as scrap paper on the regular market.

S. D. WELLS: That depends on the market situation. Our price for paper is stabilized much more than the price of waste paper which may vary all the way from $3.00 to $18.00 a ton in the course of two or three months. Our price for the books is contracted for for quite a period of time. We never pay as little as $3.00 a ton nor as much as $18.00 or $20.00, so that much of the time we are probably paying a dollar or two more per ton for our paper than the average price of the paper on the market.

CHAIRMAN DORR: If there is no further discussion we will proceed to the paper, "Water Vapor Refrigeration," by Mr. Paul Bancel, of the Ingersoll-Rand Company.

WATER VAPOR REFRIGERATION †

By PAUL BANCEL *

Curiously enough the first refrigeration machine was of the vacuum type. It was invented by Dr. William Cullen in 1755, ten years before the invention of the Watt Steam Engine, and about forty years after the early Newcomen Engines were installed in collieries at Griff and Newcastle.

William Cullen's refrigerating machine consisted of an air pump for exhausting a receiver wherein water, ethyl alcohol, nitrous ether, and other fluids were evaporated under vacuum. It will be remembered that the Newcomen Engine was an atmospheric engine in which a vacuum was produced under the piston by injecting water into the steam and absorbing its heat. Cullen's discovery that water could be made to boil in a vacuum, with extraction of heat or refrigerating effect, led to the discovery by Dr. Black of latent heat and the reversability of boiling and condensation.

Cullen's work was never carried beyond the laboratory stage. In fact it was only after eighty years that the American Jacob Perkins, applied Cullen's discovery in a compression system using ethyl ether. This became the forerunner of the systems which we have today using numerous volatile refrigerants.

Text books and handbooks invariably dispose of the water vapor system as impractical, citing the extremely high vacuums that must be maintained against the handicap of air leakage, the enormous volume of vapor per unit of refrigeration compared to other systems and the implied excessive bulk, cost and complication. These difficulties arise from the fact that water is a decidedly non-volatile refrigerant; at mean atmospheric pressure it boils at 212° and even at very high altitudes its boiling point is reduced only to about 160°. To reach a boiling point of 50°, it is necessary to reduce the pressure to 0.36 inches of mercury or a vacuum close to the barometer. Under these conditions the specific volume of water vapor is over 1700 cubic feet

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† Patents are pending on several of the new developments reported herein. —Editor.

per pound and a displacement of about 350 cubic feet a minute is required per ton of refrigerating effect (200 B.t.u. a minute).

The development of water vapor refrigeration has therefore depended in turn on the development of compressing units capable of sweeping very large volumes of low density vapor. These have taken two forms: the steam jet booster and the centrifugal compressor.

Steam Jet Refrigeration

The use of steam ejectors for compressing water vapor was suggested by Sir Charles Parsons about thirty years ago. In an early

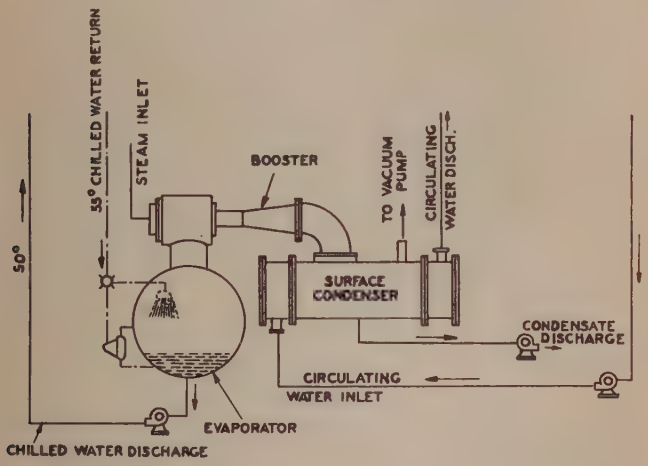


Fig. 1

patent he states that his invention consists of employing vacuum intensifiers (boosters) of the steam jet type, arranged to affect cooling by evaporation of water vapor from the body of the water to be cooled. Commercial development of Parson's idea was probably delayed by the inefficiency of the boosters available; even as recently as five years ago steam consumption was relatively high and the back pressure attainable decidedly low, compared to present day good design.

Steam jet refrigeration consists of apparatus shown diagrammatically in Figure 1 in which the water vapor boiled off at low pressure is compressed by ejector action of a steam jet and discharged at a pres-

sure high enough to permit condensation by water of ordinary temperature. It would be physically possible to compress vapors all the way to atmospheric pressure using a relatively enormous quantity of steam in successive boosters. This is unnecessary, however, because with either natural or artificial supplies of cooling water, it is possible to condense the steam at around 28″ vacuum or 2″ absolute pressure.

In addition to the steam jet booster, the apparatus of Figure 1 consists essentially of an evaporator and a condenser with auxiliary air pump. The water to be cooled is sprayed into the evaporator. If the water enters at 55° and the absolute pressure within the evaporator is maintained at .36 inches of mercury, which corresponds to a boiling point of 50°, then it is obvious that evaporation must take place until the water is cooled to 50°. Tables of the properties of steam or water vapor show that the amount of evaporation is approximately one-half per cent to obtain 5° cooling. The evaporation loss is replaced by make-up water supplied from an outside source or by the return of condensate from the main condenser.

For each pound of water evaporated, about 3 lbs. of steam must be used in the booster jet and accordingly the total discharge of compressed steam and vapors amounts to about 4 lbs. The foregoing figure for steam consumption is used for illustration only; the actual quantity of steam will vary widely with existing conditions.

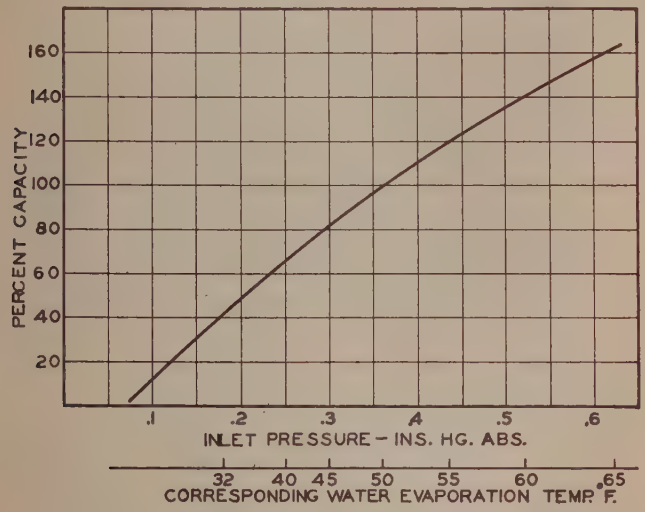
The mixture is condensed by the condenser shown at the right, which is the third major part of the apparatus. This can be of either the surface, barometric or ejector type. The necessary pumps and air removal equipment are fitted as required for the particular service. The surface condenser is probably used most frequently.

The heart of the system is the steam jet booster. Steam issues from the nozzles at velocities of 3500 to 4500 feet a second, draws in the cold vapors by aspiration and compresses the entire mass within the throat and diffusor of the ejector. Design is based largely on experiment; the proportions, size and arrangement of the essential parts have a vital influence on the capacity and compression range per pound of steam used. It is essential therefore that complete test facilities be available to the designer and, as boosters for steam jet refrigeration may readily run into large sizes, the testing facilities are necessarily elaborate.

Economy

The popularity of steam jet refrigeration rests primarily on the advantage of direct evaporation without a chemical, on simplicity, low up-keep cost, and absence of moving parts. However, where steam and water are available at ordinary costs, the economy of operation is frequently an important advantage.

It is not the author's purpose in this paper to present tabulations of the annual expense with different types of refrigerating plants as



CAPACITY CHARACTERISTICS
STEAM JET BOOSTER

FIG. 2

in his experience such comparisons must embrace too many premises as to costs, local conditions, nature of load and service, to have any useful purpose. In general, with steam pressures of 100 pounds or more a steam consumption of 25-30 pounds per ton may be assumed. If steam is worth 25 cents to one dollar a thousand pounds, ten pounds are worth ¼ cent to a cent and the hourly cost of steam is on the order of ¾ of a cent to 3 cents per ton. A mechanical refrigeration unit may be assumed to require about one horsepower per ton, and if motor driven, a power input of less than a kilowatt. Depending on the cost

of power, the hourly cost may again be anywhere from a fraction of a cent to 3 cents per ton.

If low pressure steam is used the steam consumption of the boosters is considerably greater, but the steam less expensive. In any case, the total seasonal expense depends also on the nature of the load, the response of the unit to partial loads, the nature and cost of water supply, and the important elements of first cost and fixed charges, all of which are subjects for study in individual installations.

Operating Characteristics—Steam Jet Boosters

The capacity of a given booster ejector, that is the pounds of water vapor or other gas, drawn in and compressed at fixed suction

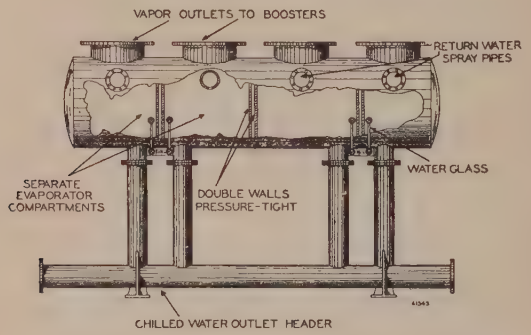


Fig. 3. Ingersoll-Rand Evaporator—showing the separate compartments for each of the boosters.

pressure is approximately constant regardless of the amount of steam being used. This fact is usually hard to grasp; Figure 2 shows a typical characteristic at normal steam flow; the capacity at 50° for example is 100 tons, if now the steam pressure on the jets is raised 25 lbs. and the steam flow in proportion, the capacity at 50° remains 100 tons. It should be emphasized that reference is made to a fixed booster which is operated with steam at different pressures, not to a series of boosters designed for the different pressures and steam flows.

To save steam therefore under varying load conditions multiple units are used with hand or automatic control to shut off one or more boosters. An arrangement with four boosters is common in units of larger size. The drawing of Figure 3 shows the design.

Manifestly, with multiple boosters some provision must be made to prevent short circuiting of the vapors from the condenser through a non-operating jet and back to the evaporator. One solution is to use large isolating valves in the booster suctions; another to subdivide the condenser into tight compartments.

The design developed by the author's Company is shown in Figure 3. All of the booster jets discharge in parallel to a single condenser, but each jet operates on its individual compartment in the evaporator. Each compartment is fitted with individual spray devices for the water

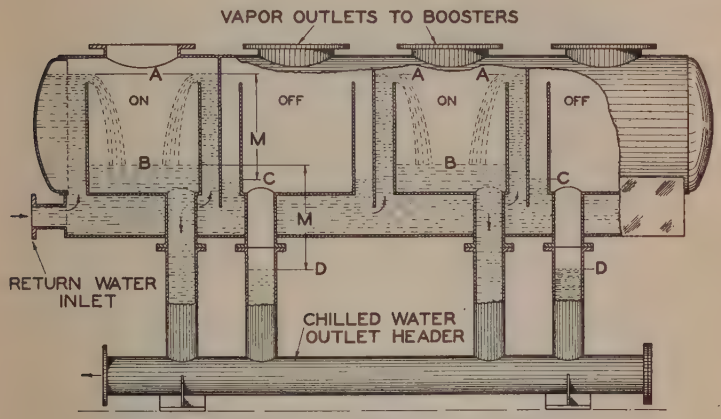

VAPOR OUTLETS TO BOOSTERS
A
ON
OFF
M
B
C
D
RETURN WATER INLET
CHILLED WATER OUTLET HEADER
A-LEVEL OF RETURN WATER OVER WEIR OF ACTIVE SECTION.
B-LEVEL OF CHILLED WATER IN ACTIVE SECTION.
C-LEVEL OF RETURN WATER BELOW WEIR OF INACTIVE SECTION.
D-LEVEL OF CHILLED WATER IN OUTLET LEG OF INACTIVE SECTION.
M-HEAD OF WATER EQUIVALENT TO DIFFERENCE BETWEEN EVAPORATOR VACUUM AND CONDENSER VACUUM.

FIG. 4

to be chilled and with individual loop seal outlet pipes leading to the chilled water removal pump.

The evaporator compartment of any jet that is not in operation is at condenser pressure, but as this compartment is isolated, it does not affect the operation of the active jets. To turn on a jet, it is necessary to turn on the steam and open the corresponding water and vent valves.

In the unit of Figures 4 and 5 further improvements have been made eliminating all but the steam valves. Opening or closing a steam valve automatically controls the water flow to the corresponding com-

partment. The diagram of Figure 4 explains the design. The water enters each compartment over weirs and when a booster is shut off the condenser pressure now exerted in the compartment depresses the water so that it cannot flow over the weir but is trapped. Turning on a booster creates higher vacuum and draws the water up so that it sprays over the weir into the chamber. This design is simple and

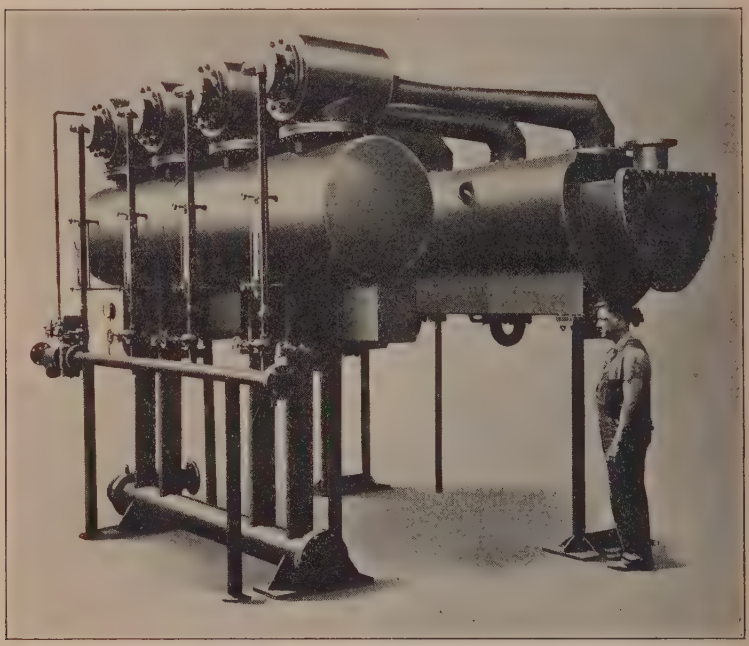


FIG. 5. A 100-Ton Refrigerating Unit for a prominent hotel air conditioning installation.

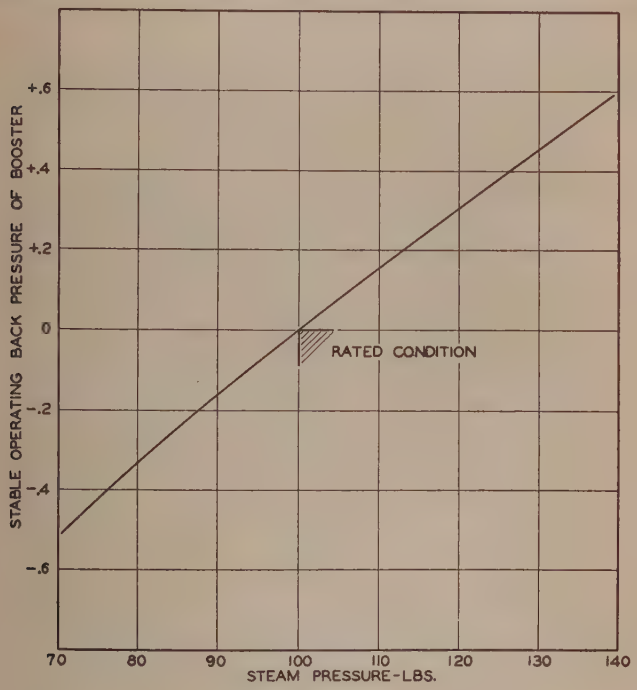
fool-proof; in the author's opinion it is the correct solution for installations subject to varying load demands.

Reserve Capacity Steam Jet Refrigeration

A steam jet refrigerating unit has large reserve capacity for small increase in chilled water temperature. If a unit is designed for 50° chilled water temperature, an increase to 55° results in a tonnage of 120% (Figure 2). In general, there is a reserve of between 4 and 5% per degree increase in temperature. This is to be contrasted with

the decidedly limited overload capacity of the conventional mechanical plant which is further discussed on page 154.

However, a refrigerating plant must not only cope with heavy tonnage demands but also excessive head or back pressures due to extremely hot circulating water. A river which shows an average



BACK PRESSURE CHARACTERISTICS
STEAM JET BOOSTER

FIG. 6

maximum temperature of 85° may at times heat up to 90°, or a cooling tower designed for high wet bulb temperature may nevertheless deliver water 5° hotter than normal maximum under unprecedented weather conditions.

At such times a mechanical unit requires excess power and falls off in tonnage produced or for full tonnage produces higher chilled water temperatures. A 5° increase in condensing water temperature

and an increase of corresponding amount in head pressure, will increase power consumption, the exact amount depending on the design and refrigerant used; at the same time the reduction in tonnage due to reduced volumetric efficiency and increased heat of liquid will be appreciable and to restore full tonnage the increase in chilled water temperature may be several degrees or more.

Under similar conditions of excess back pressure a steam jet unit may fail to function entirely. This characteristic is inherent in the nature of compression by kinetic action.

If the condenser is designed for 85° water and 2″ back pressure an increase to 90° would reduce the vacuum, or increase the back pressure to 2.3″. With .36 evaporator pressure the ratio of compression demanded of the booster is thus increased from 5.5 to 6.35, which is beyond a commercial leeway of design. By this is meant that a manufacturer bidding originally with this amount of compression ratio in reserve, would find his steam consumption guarantees criticized and his design considered inferior.

The steam jet booster will therefore break back, that is, it will be unable to compress its own burden or even a small quantity of vapor through the new and higher range of compression. This instability will continue until the evaporation pressure has increased by a relatively large amount and the chilled water temperature is 10 or 20° hotter.

Reserve against instability or failure of this type lies in an increase of steam pressure. As shown in Figure 6 every increment in steam pressure results in a corresponding increase in back pressure against which the booster jet continues efficient operation. A typical example is given in the following table; an increase from 125# gauge to 150# gauge results in stable operation of the jets against a back pressure of 2.3″ as against 2″. The steam flow is increased about 17%. For comparison with the mechanical plant, the chilled water temperature may now be increased about 2½° as shown in the last column. Under this condition the tonnage is increased by about 10%.

	Designed Max. Condensing Water Temp.	*Extreme Max. Condensing Water Temp.*	
Condensing Water Temp.	85	90	90
Back Pressure	2″	2.3″	2.3″
Chilled Water Temp.	50°	50°	52½°
Steam Press. Lbs. Gauge	125	150	150
Steam Flow (approx.)	100	117	117
Tonnage	100%	100%	110%

The unit therefore has a very desirable characteristic of increased tonnage capacity under conditions of extremely hot condensing water and high back pressure which are most likely to coincide with heavy tonnage demands. However, the heat load has been increased by the added steam flow and also slightly by the added tonnage and the condenser therefore would not produce the back pressure of 2.3″ unless it were designed to do so. A larger quantity of water so as to maintain the same temperature rise, and additional surface in the condenser as originally installed, would combine to take care of these peak conditions.

In some cases the additional tonnage may not be desired under the peak water conditions, or with cooling towers, it may not be desirable to supply sufficient capacity to cope with the added heat load. In such cases the heat quantity can be maintained at normal by shutting off one of the booster jets. In this way the added steam flow due to raising the steam pressure is off-set by deliberately closing part of the steam nozzles and the necessary tonnage load accommodated by increase in chilled water temperature. As the over-load capacity is great for a small increase in chilled water temperature, any standard subdivision of the boosters will usually be found sufficiently flexible for all the variations in operating conditions that may be encountered.

In summary, it is desirable to repeat the two important characteristics of steam jet refrigeration:

First—there is an inherently large reserve tonnage capacity. Under such conditions the chilled water temperature increases only a comparatively small amount.

Secondly—high condensing water temperature must be counteracted by reserve steam pressure. Unless all extreme conditions can be safely predicted, the apparatus should be initially designed with a reserve of 25 to 50# of steam pressure. Under extreme conditions the steam pressure is raised, and at the same time if the added heat tends to overload the condensing water supply, the steam quantity is reduced by deliberately shutting down one of the boosters.

Centrifugal Refrigeration

In the Centrifugal Unit a Centrifugal Compressor of large capacity takes the place of the steam jet boosters. The heat discharged to the condenser is therefore only the refrigeration load, plus the work of the compressor as with the ordinary refrigerating cycle.

The water vapor cycle, as mentioned, is extremely old. While en-

gineers have frequently remarked that water was a logical refrigerant and speculated on its possibilities, the author's Company was unique in having within its own staff the talent and experience required for actual construction of such a machine. Two groups of engineers were primarily concerned; experts in centrifugal compression and experts in condensation and high vacuum.

The turbo compressor engineers had built hundreds of centrifugal machines for air and gases, for pressures as high as 110 lbs., for capacities of over 100,000 feet; of one to fifteen stages, operating at 2,000 to 15,000 revolutions. However, the problem in the present case could not be solved by the mere adaptation of one of these compressors.

An enormous volume of highly attenuated water vapor had to be compressed to a pressure compatible with ordinary condensing water supplies. Since there would be no burden of steam load as with steam jets a somewhat better vacuum or lower back pressure could be expected with the Centrifugal machine and the possible discharge pressures were set down as 1½ to 2″ absolute (28 to 28½″ vacuum). While these pressures might appear low, the ratio compared to a suction pressure of say 0.36″ was surprisingly high—4½ to 6 times. This called for severe duty in the compressor.

In terms of a Centrifugal Compressor working with atmospheric intake, these ratios were equivalent to discharge pressures of 50 to 75# gauge. A compressor for 100 tons would need to have about 35,000 cu. ft. capacity and such a machine were it built to operate with atmospheric air, discharging at 50 to 75# pressure, would require as many as 10 stages and 5,000 to 7,000 horsepower driving power. Manifestly such a machine would be entirely unsuited for compressing 35,000 cu. ft. of low pressure vapor requiring less than 100 horsepower. Furthermore, it was not to be expected that highly attenuated water vapor would behave in the same way as air or gases for which the design factors were well known. Considerably less compression could be expected with water vapor than with air. To add to the difficulty it was imperative that the machine be absolutely tight against air leakage in all joints and stuffing boxes. It is little wonder that the water vapor cycle has been considered a theoretical curiosity.

The condenser while small as compared to ordinary power house units presented rather difficult and unusual problems. The discharge vapor would be superheated and condensation under these conditions was known to be difficult. A relatively high vacuum or low absolute

pressure had to be maintained when using a minimum of condensing water and air removal power. The low water consumption called for sufficient equivalent tube length or number of passes so that the water would be heated as closely as possible to the vacuum temperature. The efficient removal of the unavoidable air leakage called for counter current cooling to as near inlet condensing water temperature as possible.

Enough has been said to sketch the complexity of the problem and

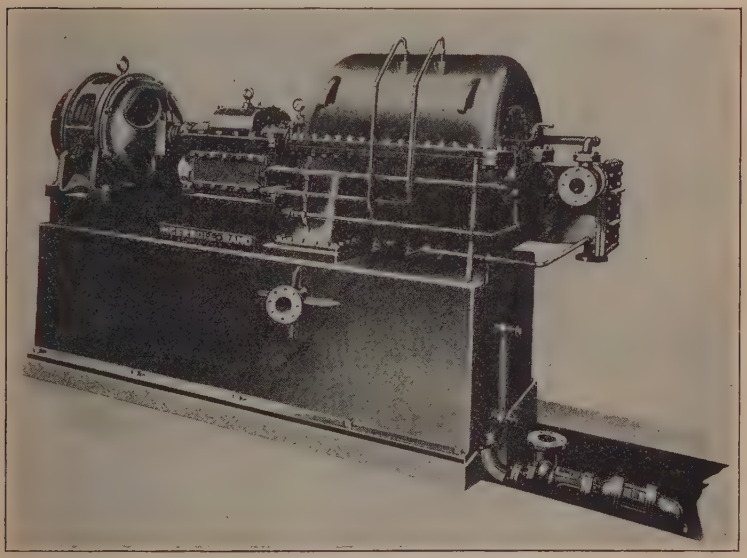


FIG. 7

the numerous difficulties confronted. The mere assembly of the component parts then available would be ridiculously impractical, costly, and inefficient. Each problem, however, was reconsidered in the light of the specific application, and the solutions developed combined into a full size experimental plant at the Phillipsburg Works of the Ingersoll-Rand Company. The compressor was turbine driven, and of large capacity. Suction and discharge were at the top; the evaporator was cylindrical and fitted in various ways for studies of water distribution, separation, and removal. The condenser was above the evaporator and of the multi-pass counter current type.

Extensive experiments were conducted. It was demonstrated that the cycle was entirely practical and the anticipated reactions to load variations proved. The result was a commercial machine illustrated in Figure 7, and the drawing of Figure 8. The compressor is set upon a base which also forms the evaporator and the condenser is attached to the compressor discharge, thus producing a compact simple assembly. No detailed description of the machine shown is necessary. Standard sizes ranging from 50 to 300 tons are available. Instead of the motor with speed-up gear a direct drive turbine can be

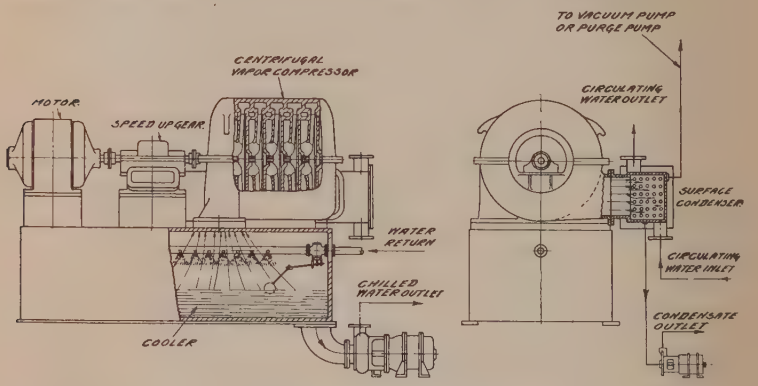


FIG. 8. Diagram showing operation of Ingersoll-Rand centrifugal vapor refrigeration system.

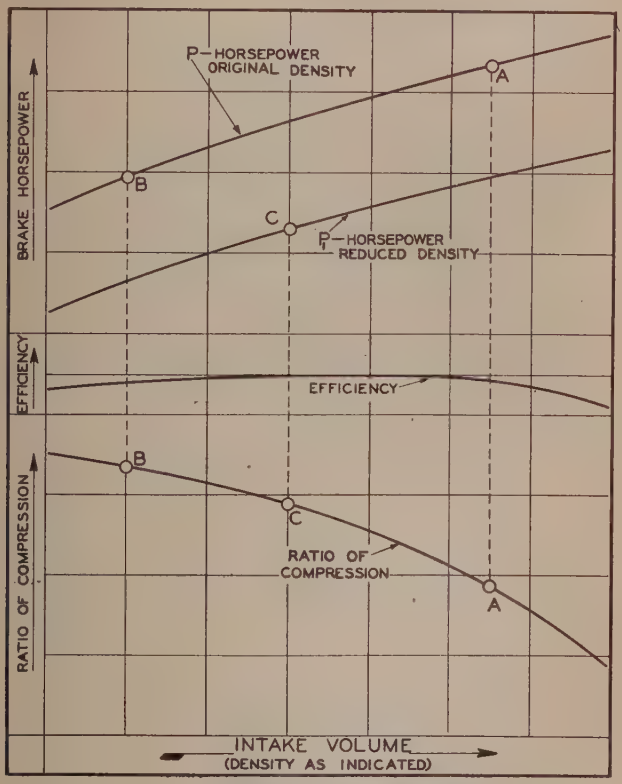
used. Speeds are from approximately 7,000 to 10,000 revolutions depending on size, which agree with recent practice in high efficiency small turbine design.

Economy

The theoretical power consumption for adiabatic compression of water vapor from 50° to 86° (the refrigeration standard) and alternatively to 95° for example, are given below:

	Suction Temp.	*Saturated Discharge Temp.*	*Adiabatic Hp. per Ton*
Water Vapor	50°	86°	(.371)
" "	50	95	(.476)
Ammonia	35	86	(.548)
"	35	95	(.658)

The theoretical horsepower requirements with ammonia are given for comparison at suction temperatures of 35°. Due to the direct evaporation of water at 50°, the theoretical horsepower is markedly less than with ammonia, which in turn is the lowest of all common refrigerants.



OPERATING CHARACTERISTICS
CENTRIFUGAL VAPOR UNIT

FIG. 9

The brake horsepower requirements of actual refrigerating units involve many factors of design and proportion; of these the efficiency of the compressor itself is probably most important, and there can be no question of the fact that a Centrifugal Compressor is usually less

efficient than a reciprocating machine. This, however, is offset in this instance by the lower theoretical power. As a result the brake horsepower requirements of the Centrifugal Unit may be said to compare favorably with any type of refrigeration, frequently being less.

Operating Characteristics

The Centrifugal Water Vapor Unit differs fundamentally from all other types in its part load characteristics. In general, the Centrifugal Unit is operated at constant speed. Under this condition and without any other adjustments, reduced tonnage is automatically reflected in reduced power, approximately in proportion to the tonnage. The unit simply floats on the load.

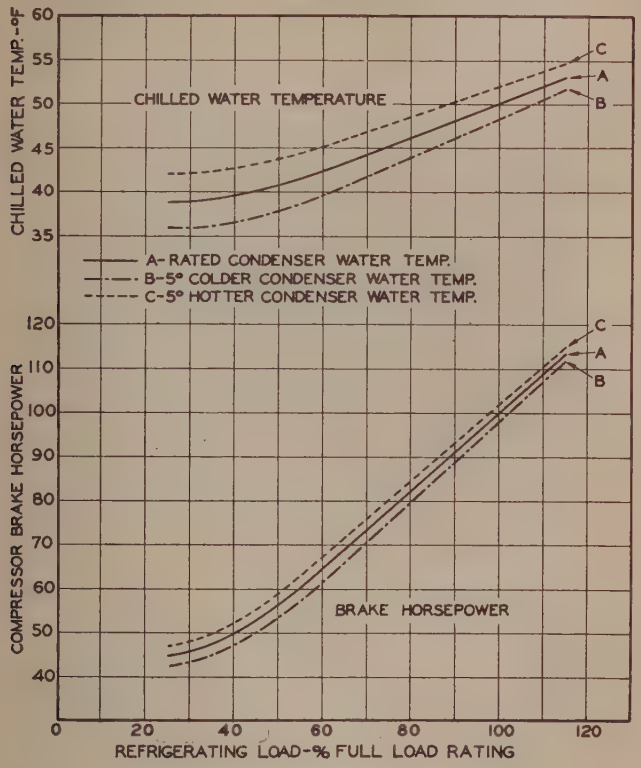
This remarkable feature of the Centrifugal Vapor Unit has been fully verified in test and commercial operation. It follows from certain fundamental relations of evaporator, compressor, and condenser, and the interrelation of their characteristics.

Figure 9 shows a typical volume characteristic of a Centrifugal Compressor: as the volume decreases the ratio of compression increases, and over the designed range, there is a flat efficiency curve. The power is shown by line P; at part volumes the brake horsepower decreases but not proportionately. A second line P_1 below P shows the power for vapor of lower density. Within limits, a decrease in density at fixed volume results in an equivalent reduction in power. Now, with decreasing load, a change occurs in both volume and density but for simplicity they can be considered as if there were two distinct phases or steps.

1. First, a decrease in volume proportionate to the decrease in load as from A to B. The power then decreases along the curve P from point A to B.
2. Second, a decrease in density and increase in specific volume which now increases the total volume to intermediate value C. However, due to the lower density, the power is now determined by lower line P_1 and the absolute value at C is less than at B.

Decreased density at reduced load is the result of reduced suction pressure which in turn is due first to the greater ratio of compression which the compressor can generate at reduced volume. Secondly, in most cases the condenser pressure decreases with reduced load and

as this is reflected at the suction of the compressor the evaporator pressure is further reduced with further reduction in density. In fact, there is frequently a cumulative effect because there is a tendency for the temperature of the condensing water to be colder at times of



OPERATING CHARACTERISTICS
CENTRIFUGAL VAPOR UNIT

Fig. 10

part loads, particularly in the case of small supplies or where cooling towers are installed. The three factors—the greater compression ratio available, the lighter heat load on the condenser and the colder condensing water, singly or combined, tend to reduce suction pressure and density.

The characteristics plotted against tonnage are shown in Figure 10. Condensing water quantity is maintained constant for all three curves of each group; in each group the center line corresponds to rated maximum condensing water temperature, the upper one an extreme maximum 5° hotter and the lower one an average 5° lower. Horsepower and chilled water temperature are seen to be approximately parallel straight line functions of the tonnage.

If constant chilled or return water temperature is desired in a process, this can be readily obtained by mixing. For example, suppose that the full load conditions are 500 GPM cooled from 55 to 50° and that 55° return water is desired at a part load; assume further that this part load corresponds to the 45° capacity point of the machine; then only part water is admitted to the evaporator and chilled from 55 to 45° the remainder of the 55° water being mixed with 45° water under thermostatic control. To make clear what is occurring it should be remembered that the quantity of chilled water has no influence of itself on the load; the tonnage is determined by the product of quantity admitted to the evaporator and the range of cooling.

In a great many processes, however, the lower water temperature is highly desirable in increasing output, or improving quality. In air conditioning the lower dew point attainable is nearly always desirable. In all such cases the machine is simply allowed to float on the load without any by-passing or mixing.

Reserve Capacity Centrifugal Unit

It was shown in connection with the steam jet unit that only a small increase in chilled water temperature occurs at overloads. A similar characteristic is true of the Centrifugal machine. In the first place, at constant intake volume the weight of vapor compressed will increase with temperature and density as follows:

$$\begin{aligned} &50°\text{—Specific Volume} && = 1700 \text{ cu. ft./lb.} \\ &55°\text{—} \quad \text{“} \quad \text{“} && = 1430 \quad \text{“} \quad \text{“} \quad \text{“} \\ &\text{Per cent weight at } 55° = \frac{1700}{1430} = 119\% \end{aligned}$$

Actually, however, the tendency with fixed condensing water conditions is for the volume compressed to actually increase, because the higher suction pressure tends to reduce the ratio of compression de-

manded. The actual increase in capacity for 5° increased chilled water temperature is therefore more nearly 25% than 19%. It follows the straight line relationship of Figure 10. For a moderate overload the increased chilled water temperature is very slight—a few degrees.

This is to be contrasted with the very sharp increase in chilled water temperature in the case of machines using a refrigerant. A small overload may readily increase chilled water temperature 10°. Two fundamental differences will be seen to account for this:

First, the change of density with increased temperature is more rapid with water vapor than any common refrigerant. This means that for a given increase in temperature, the weight compressed by a machine of fixed volumetric capacity increases in greatest proportion, with water vapor. Ammonia, Dichlorodifluoromethane (Freon), Methyl Chloride, etc., all exhibit about the same proportionate density changes with saturation temperature and the comparison with water vapor is as follows:

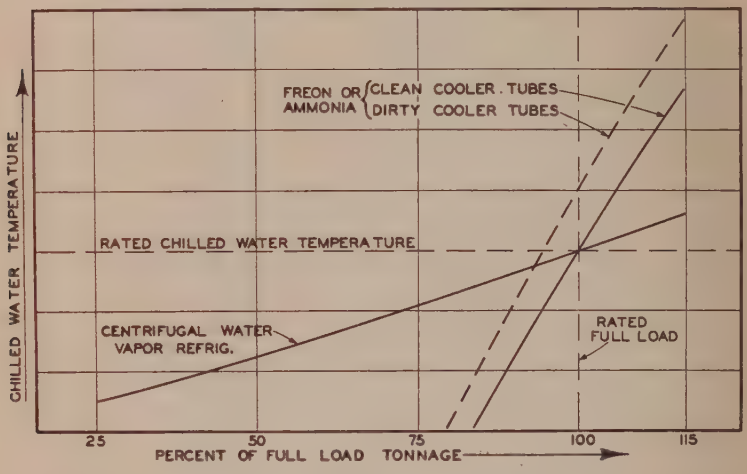
	Percentage Increase in Weight per Cubic Foot		
	Water Vapor	*Ammonia*	*Freon*
Increase in Chilled Water Temp. 50° to 55°.	19%	——	——
Increase in Refrigerant Temp. 35° to 40°..		10%	9%

In the second place, the heat of the chilled water must be transferred through tubular surface and any increase in load must be reflected in increased temperature difference; that is, the water must be hotter relatively to the evaporating refrigerant in order to transmit the greater amount of heat.

In addition, a third influence should be considered—the effect of scale or fouling on the efficiency of heat transfer. This tends to decrease the capacity at fixed chilled water temperature and also to increase the steepness at which the temperature increases with load. Figure 11 shows the comparison of the characteristics of the conventional refrigerating machine with the Centrifugal Water Vapor type.

Reserve capacity against excessive temperature of condensing water with the Centrifugal Vapor Unit has already been shown by Figure 10 in which lines "C" are for hot water. The effect of a 5° increase in condensing water temperature is a corresponding increase in condensing pressure which is reflected in higher absolute pressure

in the evaporator. This increase in suction pressure reduces the vapor volume, however, and the ratio of compression attainable increases; this counteracts severe increase in evaporator pressure and temperature. The chart shows the increase in chilled water temperature for 5° excessive condensing water temperature and it is particularly noticeable that the spread actually decreases at the heavier loads. The horsepower curves also tend to converge.



OVERLOAD CHARACTERISTICS
CENTRIFUGAL WATER VAPOR UNIT
VS
FREON OR AMMONIA UNIT

FIG. 11

Application

Standard Steam Jet or Centrifugal machines are not designed for cooling brine or for producing freezing temperatures. Temperatures from 35° up can usually be obtained but in general low temperatures should not be specified except for part load. A chilled water temperature around 50° is the normal rating of water vapor units. While the overload characteristics are remarkable and highly valuable, the author wishes to emphasize strongly the futility of underestimating operating conditions in the expectation that any machine can make up for the users' carelessness in selection. Tonnage can be rated closely, but should not be underestimated. Maximum condensing

water temperature should be definitely anticipated and specified; this is particularly true with cooling towers and ponds which in the author's experience tend to be rated on more favorable wet bulb temperatures than may actually prevail for appreciable periods of time. This is all the more important if the greatest tonnage is most likely to occur at times of extreme atmospheric conditions, thereby producing cumulative effects.

Highly attenuated vapors other than water vapor can be compressed by either steam jets or centrifugal boosters; it must be remembered, however, that the discharge pressures are still relatively low, 1½ to 2 or 2½ inches and that they are attained by condensation; it is generally necessary therefore to confine applications to condensible vapors only. It is the author's belief that other applications besides water vapor refrigeration are possible in many industrial processes where it is desirable to raise the pressure and heat level. One such application is in low temperature evaporation where vapor can be recompressed and returned to the system.

Discussion

Paul Bancel (preceding presentation of paper): Mr. Chairman and Gentlemen—I wish to exhibit a photostat of the paper by Dr. Cullen in 1755 on refrigeration. I became interested in the subject and arranged with our London office to go over to the British Museum and obtain a photostatic copy of this paper and if any of you gentlemen would like to see it, you may do so after the meeting. It is difficult to appreciate the vision of men like Dr. Cullen. He invented refrigeration before latent heat was discovered or, to put it the other way, it was his discovery of refrigeration, coupled with the work of Newcomen on the steam engine that brought about the discovery of latent heat by one of Dr. Cullen's pupils, Dr. Black, and all this was ten years before Watt invented his steam engine. The whole conception of latent heat and the reversibility of condensation and boiling was not known when Cullen was experimenting with refrigeration.

Chairman Dorr: Gentleman, the meeting is open for discussion of this most interesting paper by Mr. Bancel.

F. C. Zeisberg: I have two questions I should like to ask Mr. Bancel. The first has to do with the elimination of air or other dis-

solved gases from the water with which the machine is charged. What provision do you make for that?

The second question is have you attempted to use any other liquids than water in this type of machine? I have in mind methanol or ethanol; what would be the effect of substituting another liquid, boiling at a lower temperature, for the water?

PAUL BANCEL: Answering your first question, we are so accustomed to high vacuums now in our power house and marine work that the elimination of the air gives us little concern. Five or ten years ago we would have been worried about it. We use either a steam jet vacuum pump or a rotary vacuum pump and take out the air continuously. It is not a purging problem, but simply maintaining a vacuum as with a power house condensing plant.

Now, your second question—We have not tried any other gases. The possibilities of some of these other refrigerants that have low density, requiring a high vacuum, may be very great.

F. C. ZEISBERG: It seems to me from theoretical considerations that there exists a possibility here in getting a very wide range of temperatures, that is, by the substitution of either pure liquids for the water or from the use of isopropyl mixtures containing water or combination of other solvents of water.

H. W. MAHR: I would like to ask whether you have applied this system to the specific problem of crystallization, vacuum crystallization, and if so, how it is modified, and if the jet or the mechanical system is best adapted for that work?

PAUL BANCEL: We have not so far as I know.

J. W. LIVINGSTON: With regard to the steam jet and the centrifugal compressor, what in your opinion is the field of each? Supposing, for instance, you had steam at 100 or 120 pounds pressure, in the case of a centrifugal compressor or steam jets, would not the choice of the machine depend on the economic use of the steam exhausted, or are there other factors that would govern that?

PAUL BANCEL: Well, the trouble is that sometimes it is not economics. I can make neither head nor tail out of the steam rates that some of the street steam companies are selling their steam at for summer use. In some cases the steam appears to sell for less than cost.

CHAIRMAN DORR: I know of a building that has been put in for conditioning in New York and, due to this change in rates,—you are probably familiar with the First National Bank Building—they figured out they could save five hundred dollars by conditioning and heating over the cost of heating alone.

PAUL BANCEL: As an alternative to Steam Jet Refrigeration you can put steam through a turbine, driving a centrifugal machine and use considerably less than you would in steam jet boosters. You will pay more for the machine, but you will pay less for the cooling tower to get rid of the heat and you may run into situations where a man has not space for the cooling tower or does not want it. As to cost,

the centrifugal machine is, say, fifty per cent more than the steam jet machine.

R. J. THOMPSON: As concerns the condenser side, what is the water requirement per minute, per standard ton under the usual conditions?

PAUL BANCEL: I am not a refrigeration man, and I do not think in terms of water per ton, but I will answer your question in its elements. The amount of heat is the same, substantially, as with any refrigerating cycle. You are talking now centrifugal or steam jet?

R. J. THOMPSON: I am thinking, first, of the steam system and then the centrifugal.

PAUL BANCEL: The amount of heat with the steam jet is about three times what it is with a mechanical or centrifugal system, about 45,000 B. t. u.'s per minute per ton, as against fourteen or fifteen thousand with the mechanical system. The water requirement will not be three times as much because you can allow a larger temperature range on the water—I would say two times as much instead of three times.

The water requirement of the centrifugal machine is the same as any other refrigerating machine and there must be the same economic balance, the more water the less horse power, and the less water the more horse power.

R. J. THOMPSON: Now you spoke of the centrifugal machine as running at constant speed. In case you have a fluctuating load, how do you take care of the variations in refrigeration requirements?

PAUL BANCEL: You do not.

R. J. THOMPSON: You take just what you can get?

PAUL BANCEL: That is the beauty of the machine—it is self-regulating. At part load the volume and density of the vapor go down, and the horse power required goes down in proportion to both the density and reduced volume. Even with a turbine I do not see any need for variable speed.

D. R. KELLOGG: This is a more or less incidental question: you mentioned the great aid which welding had been in your work. I wonder if it would be fair to ask you whether hydrogen or gas welding or the coated electrode was used?

PAUL BANCEL: I think frequently the coated electrode, but we use bare electrode also.

D. R. KELLOGG: I was thinking particularly of the vacuum joints, places where you really want tightness.

PAUL BANCEL: Successive beads or layers are applied, each layer being cleaned before applying the next.

D. R. KELLOGG: It is a bead laid on from a coated electrode?

PAUL BANCEL: Yes. We do either type.

CHAIRMAN DORR: Gentlemen, is there any further discussion? If not, I am sure we are extremely grateful to Mr. Bancel for coming down here and giving us this paper, the presentation of which has been most helpful.

THE ISOTHERMAL FLOW OF LIQUID LAYERS

By C. M. COOPER,* T. B. DREW,* and W. H. McADAMS *

The use of wetted-wall towers in connection with such processes as absorption, rectification, and humidification lends importance to the relationships which describe the motion of thin layers of liquid flowing under the action of gravity over wetted surfaces. The radii of curvature of these surfaces are usually so great relative to the thickness of the fluid layer that the problem is essentially that of a broad, shallow, open stream on a flat plate. This case of flow in open channels may be found in any treatise on hydraulics, but the velocity range for which such formulae are customarily used is far above that met in the circumstances of interest here.

That turbulent or viscous-laminar motion will occur in a shallow stream, according as the velocity is high or low, has been definitely proved by the classical color-band method, as in the work of Schoklitsch (8). The general use by hydraulic engineers of the Chezy formula and its modifications in open channel computations shows that the usual laws of turbulent flow in pipes apply to turbulent flow in open channels. The Chezy formula is merely the Fanning equation,

$$\triangle h = \frac{fLV^2}{2\,gm} \quad , \qquad (1)$$

solved for the mean linear velocity V. $\triangle h$ is the drop in head over the length L; f, the friction factor; m, the hydraulic depth†; and g the acceleration due to gravity. It is necessary to determine experimentally either f or the corresponding Chezy coefficient $\sqrt{2g/f}$. For each cross-sectional shape and kind of wetted surface, f is a function of the Reynolds number,

$$Re = \frac{4mV\rho}{\mu} \quad ,$$

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† $m = \frac{1}{4}$ diameter for a full circular pipe; m = actual depth for a shallow stream; in general m is the ratio of the cross-section of the stream to the wetted perimeter.

where μ is the absolute viscosity and ρ the density of the fluid. Usually, in turbulent flow past smooth surfaces f is substantially the same function of Re whatever the cross-sectional shape. An exception might arise in the present case if the contiguous gas phase should exert appreciable traction at the gas-liquid interface. In the viscous range the desired formulae are contained in Lamb's Equations 4 and 10, pp. 550-551 of his "Hydrodynamics" (5th ed.)[7] which are easily derivable from the definition of viscosity. Since the pressure gradient as used by Lamb in these equations is to be understood as the sum of the static pressure gradient and the effective gravitational force per unit volume,[7a] a simple change in variable makes his Equation 4 become

$$q = \frac{m^3}{3\mu} \rho g \sin \alpha \qquad (2)$$

or

$$C = \frac{m^3 \rho^2 g \sin \alpha}{3\mu} \qquad (2a)$$

where q is the volumetric discharge per unit breadth; C, the weight rate of flow per unit breadth; m, the depth of stream; μ the absolute viscosity; and α, the angle between the plate and the horizontal. Equation (2) applies when there is no traction exerted at the gas-liquid interface; when by such traction the exposed surface is maintained at a downward velocity U, the corresponding theoretical formula is

$$q = \frac{mU}{2} + \frac{m^3}{12\mu} \rho g \sin \alpha \qquad (3)$$

For both turbulent and viscous flow suitable corrections for end effects, and for change in kinetic energy must be introduced if the variation in depth is appreciable; this refinement is generally not necessary in the case of thin films.

The theoretical velocity distributions corresponding to Equations (2) and (3) are

$$u = \frac{\rho g \sin \alpha}{\mu} \left(my - \frac{y^2}{2} \right) \qquad (4)$$

and

$$u = \frac{y}{m} U + \frac{\rho g \sin \alpha}{2\mu} \left(my - y^2 \right) \qquad (5)$$

respectively, where u is the local linear velocity at distance y above the bottom of the channel. The tractive force per unit area at the gas-liquid interface in the second case is

$$T = \frac{\mu}{g}\left(\frac{du}{dy}\right)_{y=m} = \frac{\mu}{g}\left(\frac{U}{m} - \frac{m\rho g \sin \alpha}{2\mu}\right) \quad (6)$$

which acts downward when it is positive.

Comparison of the Theory with Data

For the study of the experimental data it is convenient to present the results in the form of a plot of f versus Re, so that a comparison with the known curves for pipes may be readily made. By the substitution $mV\rho = C$, which is the weight rate of flow per unit breadth, the formula used in computing f from C and the measured depth m is easily obtained from Equation 1:

$$f = \frac{2gm^3\rho^2 \sin \alpha}{C^2} \quad (7)$$

where $\sin \alpha$ has replaced $\triangle h/L$. By the same substitution, Re is seen to be $4C/\mu$, which need not involve m. Equation 2, for viscous flow with a free surface, is equivalent to

$$f = 24/Re. \quad (8)$$

Equation 8 is plotted in Figure 1 together with the friction factor curve for smooth round pipes as given by Drew, Koo, and McAdams.[4]

Various hydraulic engineers have reported measurements on the flow of shallow rivers, but apparently it is difficult or impossible to obtain results of accuracy under other than laboratory conditions (Cf., Gibson[5]. In 1910 Hopf[6] published the earliest results found of use in the present study. He investigated the flow of water and of sugar solutions along a slightly inclined, polished brass trough, 5.2 cm. wide by about 40 cm. long. The depth was measured by a micrometer. The slopes ranged from 0.008:1 to 0.059:1. Except for the smallest depths, the narrowness of Hopf's trough renders the data unsuited for testing the present theories. These theoretical equations are not applicable when the depth is appreciable relative to the breadth of the stream. Moreover, in high velocity runs ripples originating at the edges made the measurement of layer thickness uncertain. Never-

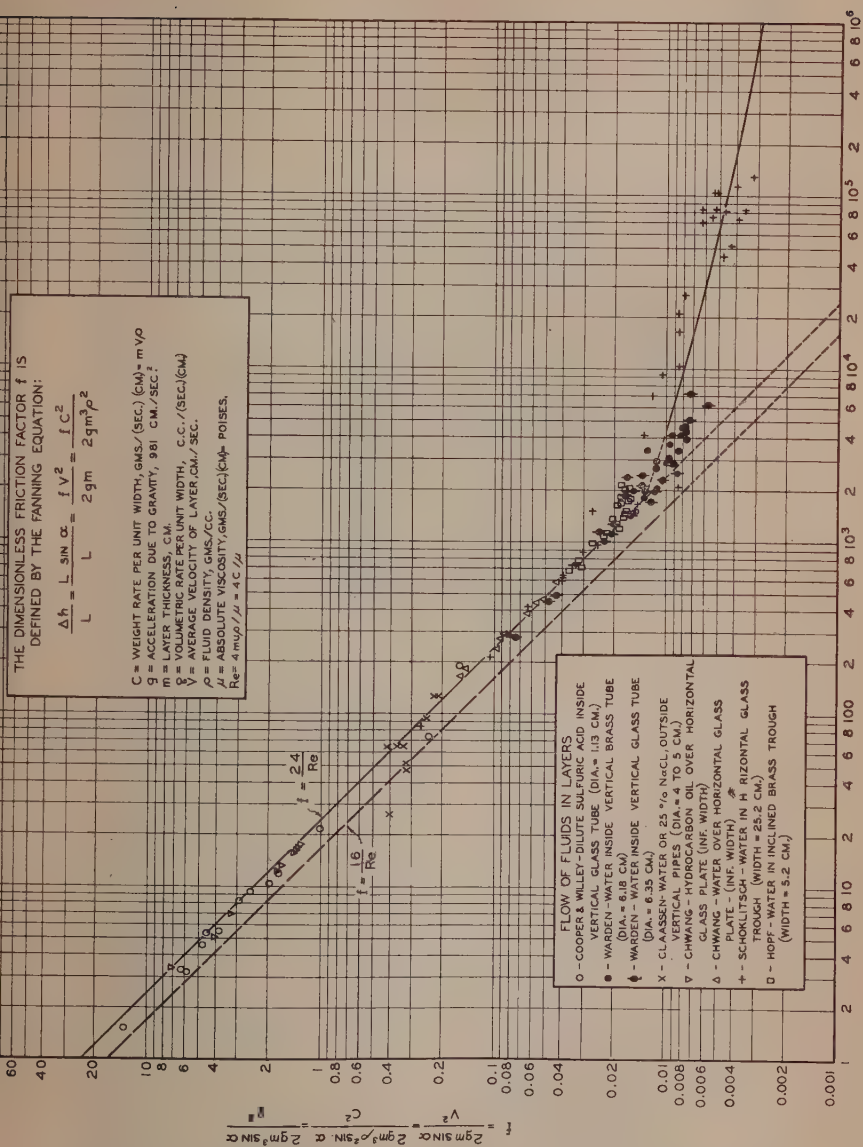
THE DIMENSIONLESS FRICTION FACTOR f IS DEFINED BY THE FANNING EQUATION:
$\frac{\Delta h}{L} = \frac{L \sin \alpha}{L} = \frac{f V^2}{2gm} = \frac{f C^2}{2gm^3\rho^2}$
C = WEIGHT RATE PER UNIT WIDTH, GMS./(SEC.)(CM.) = m Vρ
g = ACCELERATION DUE TO GRAVITY, 981 CM./SEC.²
m = LAYER THICKNESS, CM.
β = VOLUMETRIC RATE PER UNIT WIDTH, C.C./(SEC.)(CM.)
V = AVERAGE VELOCITY OF LAYER, CM./SEC.
ρ = FLUID DENSITY, GMS./C.C.
μ = ABSOLUTE VISCOSITY, GMS/(SEC.)(CM.) POISES.
$Re = 4m\rho/\mu = 4C/\mu$
FLOW OF FLUIDS IN LAYERS
O - COOPER & WILLEY - DILUTE SULFURIC ACID INSIDE VERTICAL GLASS TUBE (DIA. = 1.13 CM.)
● - WARDEN - WATER INSIDE VERTICAL BRASS TUBE (DIA. = 6.18 CM.)
◐ - WARDEN - WATER INSIDE VERTICAL GLASS TUBE (DIA. = 6.35 CM.)
X - GLASSEN - WATER OR 25 % NaCl, OUTSIDE VERTICAL PIPES (DIA. = 4 TO 5 CM.)
▽ - CHWANG - HYDROCARBON OIL OVER HORIZONTAL GLASS PLATE (INF. WIDTH)
Δ - CHWANG - WATER OVER HORIZONTAL GLASS PLATE - (INF. WIDTH)
+ - SCHOKLITSCH - WATER IN H RIZONTAL GLASS TROUGH (WIDTH = 25.2 CM.)
□ - HOPF - WATER IN INCLINED BRASS TROUGH (WIDTH = 5.2 CM.)
$f = \frac{24}{Re}$
$f = \frac{16}{Re}$
$f = \frac{2gm \sin\alpha}{V^2} = \frac{2gm^3\rho^2 \sin\alpha}{C^2} = \frac{2gm^3 \sin\alpha}{\beta^2}$
REYNOLDS NUMBER = $\frac{4m\rho}{\mu} = \frac{4C}{\mu} = \frac{4\beta\rho}{\mu} = Re$
Nov. 1933.

FIG. 1. The Fanning Friction-Factor f for Liquid Layers plotted vs. the Reynolds Number. Theoretically, for streamline flow, $f = 24/Re$ on flat plates, and $f = 16/Re$ for circular pipes. The solid curve at the right is for smooth circular pipes.[4] : $f = 0.00140 + 0.125/Re^{0.32}$.

theless, a few of the data have been plotted in Fig. 1, and are in excellent agreement with Equation 8 at low Reynold's numbers.

Claassen [2], in 1918, desiring to test the assumptions of certain theories of heat transmission, studied the flow of water, of molasses, and of 25% NaCl solution down the outer vertical walls of a polished, an unpolished but bright, and a rough steel pipe. The outside diameter of the first pipe was 5.0 cm. and its wetted length was 135.0 cm.; for the other pipes the diameter was 4.0 cm. and the wetted length, 196.0 cm. The "holdup," from which the average layer thickness could be computed, was determined by stopping the flow, weighing the drainage, and adding to the weight thus obtained the weight of the liquid adhering to the surface. The latter quantity was found by wiping

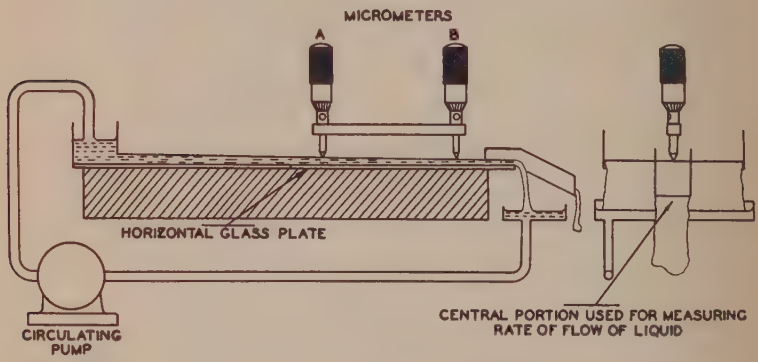

FIG. 2 The Apparatus of Chwang.

the surface with a tared towel and reweighing the towel. Unfortunately, in more than half of his runs Claassen either used molasses of unrecorded viscosity or operated at such a high inlet temperature that cooling by evaporation vitiated the results. Hence it is permissible to show but few of his data in Fig. 1. They are not very consistent among themselves, but two-thirds of the points lie close to the theoretical curve.

In 1920 Schoklitsch [8], in the course of an extensive series of experiments on the flow of both clear and muddy water in shallow streams, repeated and extended the experiments of Hopf. He used a trough 25.5 cm. wide with a plate glass floor and varnished wood sides. The data are reported only in the form of a small graph in

which the depth is plotted against the mean velocity. The slopes ranged from 0.0042:1 to 0.0340:1. A number of points have been read from the graph and transferred, after the necessary computations, to Fig. 1. In judging these data possible errors due to the method of transcription must be taken into account.

In 1928 Chwang [1], with an apparatus (Figure 2) similar to that of Hopf, measured layer thicknesses and rates of flow over a flat

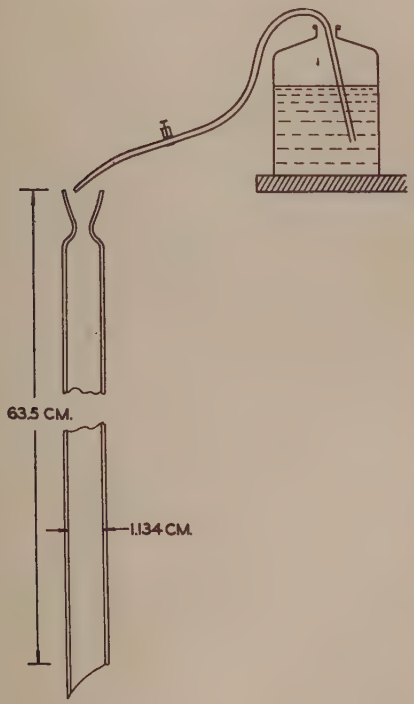

FIG. 3. The Apparatus of Cooper & Willey.

glass plate for slopes between horizontal and 0.23:1. Both water and a viscous hydrocarbon oil were used. The plate was about 10 inches wide, and to avoid edge effects the measurements were made only for a narrow strip near the center line of the plate. Uncertain end-effects render his high velocity data unsuited for the present discussion. Only runs at low velocities with zero angle of plate inclination are plotted in Fig. 1. These data are included in Table 1.

TABLE I—Experimental Data and Results

Temp. ° C.	ρ Density Gm. per cc.	μ Viscosity* Poises (gm.)/(sec.) (cm.)	sin α Slope of Free Surface	Holdup cc.	m Layer thickness	q Cc./(sec.) per cm. width	$4mu\rho/\mu = 4q\rho/\mu$ Reynolds number	$f=\frac{2\,gm^3 \sin\alpha}{q^2}$ Friction Factor
Lubricating Oil on Horizontal Glass Plane (Chwang)								
21	0.872	0.560	0.0100	.....	0.467	0.533	3.32	7.05
"	"	"	0.0104	.....	0.503	0.796	4.96	4.08
"	"	"	0.0119	.....	0.552	1.10	6.85	3.25
"	"	"	0.0135	.....	0.636	1.97	12.3	1.76
"	"	"	0.0136	.....	0.650	2.11	13.2	1.65
"	"	"	0.0143	.....	0.677	2.49	15.5	1.40
"	"	"	0.0144	.....	0.685	2.56	16.0	1.39
"	"	"	0.0147	.....	0.700	2.72	17.0	1.34
"	"	"	0.0146	.....	0.706	2.81	17.5	1.28
Water on Horizontal Glass Plane (Chwang)								
4.4	1.00	0.01548	0.00185	.....	0.270	0.697	180	0.147
"	"	"	0.00185	.....	0.283	0.920	238	0.0972
"	"	"	0.00213	.....	0.291	1.036	268	0.0957
"	"	"	0.00213	.....	0.300	1.12	290	0.0910
"	"	"	0.00230	.....	0.309	1.45	374	0.0638
"	"	"	0.00258	.....	0.317	1.69	436	0.0567
"	"	"	0.00258	.....	0.317	1.76	455	0.0520
"	"	"	0.00270	.....	0.345	2.25	582	0.0430
Dilute Sulfuric Acid Inside Vertical Glass Tube (Willey and Cooper)								
26.5	1.082	0.01105	1.00	1.076	0.00476	0.00392	1.53	13.8
25.5	1.082	0.01128	1.00	1.336	0.00590	0.00830	3.18	5.93
26.7	1.082	0.01098	1.00	1.386	0.00612	0.00845	3.33	6.35
27.7	1.081	0.01075	1.00	1.538	0.00679	0.01144	4.60	4.68
26.6	1.082	0.01100	1.00	1.650	0.00730	0.01413	5.56	3.81
26.6	1.082	0.01100	1.00	1.740	0.00769	0.01405	5.53	4.50
27.4	1.081	0.01082	1.00	1.956	0.00864	0.02087	8.34	2.89
27.1	1.081	0.01090	1.00	2.011	0.00888	0.02382	9.46	2.40
27.1	1.081	0.01090	1.00	1.995	0.00883	0.02612	10.4	1.99
27.3	1.081	0.01085	1.00	2.093	0.00928	0.03018	12.0	1.70
27.2	1.081	0.01087	1.00	2.603	0.01152	0.0547	21.8	1.00
26.5	1.082	0.01105	1.00	3.740	0.01655	0.1930	75.6	0.239
21.8	1.084	0.01230	1.00	6.520	0.0289	0.544	192.	0.159

* Viscosity of water was taken from "International Critical Tables" V, 10 (1929). For other liquids viscosity was determined experimentally.

TABLE I (*Continued*)—Experimental Data and Results
Water in Vertical Glass Tube (Warden)

Temp. ° C.	ρ Density Gm. per cc.	μ Viscosity* Poises (gm.)/(sec.) (cm.)	$\sin \alpha$ Slope of Free Surface	Holdup cc.	m Layer thickness	q Cc./(sec.) per cm. width	$4mu\rho/\mu = 4q\rho/\mu$ Reynolds number	$f = \frac{2\ gm^3 \sin \alpha}{q^2}$ Friction Factor
20	0.998	0.01008	1.00	39	0.0267	0.702	278	0.0757
20	0.998	0.01008	"	40.5	0.0277	0.706	280	0.0837
24	0.997	0.00916	"	43.5	0.0298	1.036	450	0.0484
24	0.997	0.00916	"	45	0.0308	1.146	498	0.0437
20	0.998	0.01008	"	54.5	0.0374	1.79	709	0.0321
20	0.998	0.01008	"	61	0.0417	2.49	986	0.0230
20	0.998	0.01008	"	67	0.0459	2.81	1110	0.0242
20	0.998	0.01008	"	65	0.0445	2.88	1140	0.0208
20	0.998	0.01008	"	67	0.0459	3.04	1205	0.0205
14	0.999	0.01174	"	76	0.0521	4.20	1430	0.0157
14	0.999	0.01174	"	80	0.0548	5.10	1740	0.0124
14	0.999	0.01174	"	93	0.0637	5.39	1830	0.0175
20	0.998	0.01008	"	77	0.0528	5.07	2010	0.0112
20	0.998	0.01008	"	79	0.0541	5.27	2090	0.0112
13	0.999	0.01206	"	94	0.0644	6.89	2290	0.0110
13.5	0.999	0.01191	"	89	0.0610	7.16	2400	0.0087
14	0.999	0.01174	"	96	0.0658	6.32	2150	0.0140
14	0.999	0.01174	"	96	0.0658	6.39	2170	0.0136
14	0.999	0.01174	"	100	0.0685	6.42	2180	0.0115
13.5	0.999	0.01191	"	105	0.0719	7.19	2410	0.0141
13	0.999	0.01206	"	110	0.0753	7.03	2340	0.0170
16.8	0.999	0.01093	"	132	0.0904	13.9	5070	0.0075
16.8	0.999	0.01093	"	134	0.0918	14.2	5180	0.0075
49	0.989	0.00558	"	80	0.0548	5.86	4160	0.0094
16.8	0.999	0.01093	"	140	0.0958	17.1	6230	0.0059
16.8	0.999	0.01093	"	168	0.115	20.1	7330	0.0074

* Viscosity of water was taken from "International Critical Tables" V, 10 (1929).

WATER IN VERTICAL BRASS TUBE (WARDEN)

Temp. ° C.	ρ Density Gm. per cc.	μ Viscosity* Poises (gm)/(sec.) (cm.)	$\sin \alpha$ Slope of Free Surface	Holdup cc.	m Layer thickness	q Cc./(sec.) per cm. width	$4mu\rho/\mu = 4q\rho/\mu$ Reynolds number	$f = \frac{2\,gm^3 \sin \alpha}{q^2}$ Friction Factor
30	0.996	0.00800	1.00	61	0.0411	3.00	1490	0.0152
50	0.988	0.00549	"	48.5	0.0327	2.12	1530	0.0152
40	0.992	0.00654	"	58	0.0391	2.95	1790	0.0136
40	0.992	0.00654	"	60	0.0405	3.39	2030	0.0114
50	0.988	0.00549	"	58	0.0391	2.97	1990	0.0133
30	0.996	0.00800	"	71	0.0479	4.44	2210	0.0110
50	0.988	0.00549	"	62	0.0418	3.80	2740	0.0100
50	0.988	0.00549	"	79	0.0533	6.17	4440	0.0078
40	0.992	0.00654	"	72	0.0485	4.72	2860	0.0100
40	0.992	0.00654	"	73.5	0.0496	4.85	2940	0.0102
50	0.988	0.00549	"	66.5	0.0448	4.23	3050	0.0098
40	0.992	0.00654	"	88	0.0593	5.58	3380	0.0132
50	0.988	0.00549	"	77.5	0.0523	5.91	4260	0.0081
30	0.996	0.00800	"	92	0.0620	7.10	3540	0.0093
50	0.988	0.00549	"	74	0.0499	5.06	3640	0.0095
40	0.992	0.00654	"	83.5	0.0563	6.05	3670	0.0096
40	0.992	0.00654	"	87	0.0586	6.85	4160	0.0084
30	0.996	0.00800	"	79	0.0533	5.69	2830	0.0092
18	0.999	0.01060	"	106	0.0714	7.84	2950	0.0116
17	0.999	0.01088	"	101	0.0680	7.34	2690	0.0116
28	0.996	0.00836	"	90	0.0607	7.20	3420	0.0085
35	0.994	0.00721	"	87	0.0587	7.20	3970	0.0077
45	0.990	0.00597	"	86	0.0580	6.84	4530	0.0082

* Viscosity of Water was taken from "International Critical Tables" V, 10 (1929).

Willey [3], in collaboration with one of the present authors, studied the flow of dilute sulfuric acid down the inside wall of a vertical glass tube 1.134 cm. in diameter and 63.5 cm. high, Fig. 3. The holdup was measured by stopping the flow, draining, washing out the adhering liquid, and determining the acid in the combined drainage and wash-

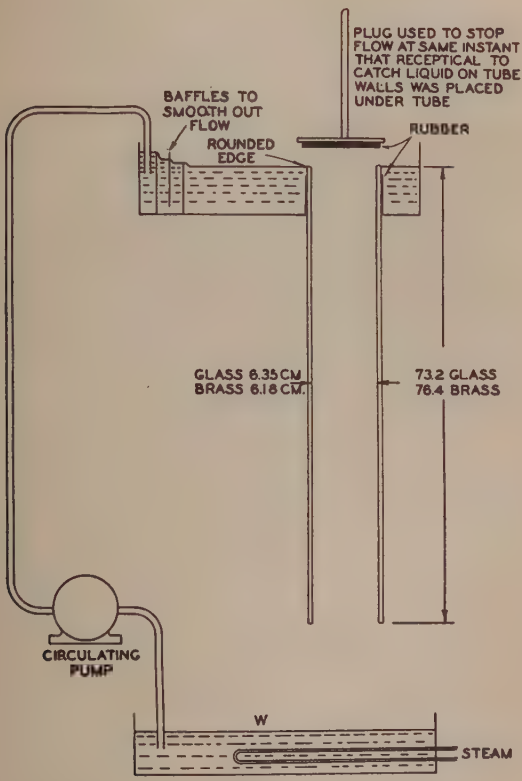

FIG. 4 The Apparatus of Warden.

ings by titration. These data are plotted in Fig. 1 and listed in Table 1. They cover the range of Reynold's numbers from 1.53 to 192 and are in rough agreement with Equation 8.

Warden [9], in 1930, employed an apparatus (Fig. 4) similar to that of Cooper and Willey, but water was the liquid studied and the

holdup was determined by a modification of the method of Claassen (*loc. cit.*). The viscosity of the water was varied by controlling its temperature, which for the data presented here ranges from 20° C. to 50° C. The Reynolds number ranged from 278 to 7330. Warden used a glass tube with a diameter of 6.35 cm. and a length of 73.2 cm., and a brass tube with a diameter of 6.18 cm. and a length of 76.4 cm.

Examination of Fig. 1 shows that the data as a whole are in excellent agreement with the theoretical Equation 8 if *Re* is less than about 1500 and this limit may be raised to 2100, the lower Reynold's Criterion in circular pipes, without doing violence to any of the more reliable measurements. For larger values of *Re* the friction factor curve given by Drew, Koo, and McAdams [4] for smooth round pipes is a fair approximation for the data. The precision of the data at present available in the turbulent flow range is believed insufficient to warrant the presentation of a separate curve for flow on plates. It may therefore be concluded that for *Re* less than 2100 the theoretical viscous flow formulae may be used when dealing with wetted-wall towers and the like, while for Re greater than 2100 the Fanning equation together with the usual friction factor curves should give results of sufficient precision for many purposes. There is no indication from the data available that gas traction at the interface between gas and liquid has any appreciable effect on the flow of the liquid film. However, since in the experiments discussed no positive gas velocity was used, the absence of such an effect in other cases can by no means be assumed. In fact it is well-known that a sufficiently high gas velocity will entirely stop the flow of a liquid film.

Nomenclature *

C = weight rate flow per unit breadth, (gms.)/(sec.)(cm.)
f = friction factor (dimensionless).
g = acceleration due to gravity, 981 cm./sec.^{2}
$\triangle h$ = drop in head, cm.
L = length of channel over which $\triangle h$ is measured, cm.
m = hydraulic depth, cm.
q = volumetric rate of flow per unit breadth (cc.)/(sec.)(cm.)
Re = Reynolds number $= \dfrac{4mV\rho}{\mu} = \dfrac{4C}{\mu}$
T = tractive force-exerted by gas on interface, gms./sq. cm.

* Any consistent set of units may be employed.

u = local linear velocity (cm./sec.)
U = downward linear velocity of interface (cm./sec.)
V = mean linear velocity, cm./sec.
y = perpendicular distance from bottom of channel, cm.
α = angle of inclination to horizontal.
ρ = density, (gms./cc.)
μ = absolute viscosity, (gms.)/(cm.)(sec.)

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HEAT TRANSFER BY CONDENSING VAPOR ON VERTICAL TUBES

By C. G. KIRKBRIDE *

Vertical tube condensers are not as common in industrial practice as horizontal tube condensers. This is due to three important reasons: namely, tube bundles cannot be "pulled" for cleaning as easily as horizontal tubes, less is known about predicting heat transfer coefficients for vertical tubes, and it is erroneously believed by many that lower coefficients of heat transfer are obtained with vertical tubes than with horizontal tubes. Where cleaning problems do not limit the design, it seems that the vertical tube condenser deserves more serious consideration and consequently an accurate method of predicting heat transfer coefficients for vertical tubes because of considerable importance. An accurate method which is valid for all rates of condensation has not yet been presented in the literature, but several excellent papers dealing with this subject have been presented. Nusselt [8] developed the theoretical equation

$$h_m = 0.943\left(\frac{k^3\rho^2\lambda g}{\mu L(t_c - t_w)}\right)^{1/4} \qquad (1)$$

for computing the average heat transfer coefficient h_m over the tube length L where the condensate flows down the tube in viscous motion. The thermal conductivity k, the density ρ and the viscosity, μ of the condensate are taken at the arithmetic average of the tube wall temperature, t_w and the condensate film surface temperature, t_c. The heat absorbed above t_c, per unit mass of condensate, is equal to the latent heat of condensation plus the sensible heat of the vapor † and is represented by λ. The accceleration due to gravity, g, is 32.2 ft./sec.^{2} (980 cm/sec.^{2}) at sea level.

Jacob and Erk [4] presented experimental results on condensing

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†Nusselt considered the special case of condensing saturated vapor, but if superheated vapor is condensed the superheat must be added.

steam on a short vertical tube (0.466 meter or 18.35 inches). They observed that Nusselt's theory gave only fair agreement. Their results which were lower than predicted by equation (1) varied 100% at times with theoretical results. Unfortunately they did not present their data in detailed form so a further analysis is difficult.

Badger, Monrad and Diamond [1] presented data taken on condensing diphenyl on a vertical tube. In a paper by Monrad and Badger [7] an attempt was made to correlate the data with Nusselt's equation (1). They pointed out that the data were at times 400% higher than predicted by Nusselt's theory. The reason for this was given as turbulence in the condensate film which Nusselt had assumed did not exist. They observed a general trend of increasing heat transfer coefficients with increasing temperature differences but were apparently unable satisfactorily to correlate the data so it could be applied generally.

Callendar and Nicolson [2] presented data taken on condensing steam inside of a short vertical tube (2 ft.) Their investigation was made in order to determine the amount of condensation in the cylinders of steam engines but the data are applicable to the present subject.

Phillips [9] made a study of vertical tube evaporators and obtained coefficients for the condensate film as incidental data. These data were never published and are not available in the literature.

Jordan [5] has presented data on a vertical tube 1 meter in length. Monrad and Badger showed that these data checked Nusselt's equation only qualitatively and were lower than the theory predicted in many cases, thus being in agreement with Jacob and Erk.

The major portion of data on condensing vapors on vertical tubes in the literature are higher than predicted by Nusselt's theory. Two different explanations have been proposed for these results. The first and probably the correct one is turbulence in the condensate film. The second is that drops form on the tube surface and upon becoming large enough drain from the tube in streams. Schmidt, Schurig and Sellschopp [10] presented pictures to substantiate this explanation. They pointed out that it was necessary, however, to have a highly polished surface or a film would form. They condensed steam on a highly polished copper surface but noticed that as the surface became slightly oxidized film condensation occurred.

Wulfinghoff [11] claims "drop forming" condensation does not exist in industry because too low a condensate rate and too smooth a surface are required. This is in accordance with observations made by the author on water, gasoline and α-bromnaphthalene. Very smooth

glass tubes were used but "drop forming" condensation occurred only with steam and that at very feeble condensate rates. Since in industrial practice, low condensate rates are not common, the possibility of drop forming condensation is not favorable.

It was observed that at the top of the tubes clear films existed and a few inches from the top the formation of ripples or waves began. Upon approaching the bottom the waves became closer together until near the bottom the films were in a violent disturbance which had the appearance of turbulence.

Since the literature contains so little information on condensation on vertical tubes and on liquid films flowing down vertical surfaces, it was decided to investigate this subject and attempt to develop a reliable method for predicting heat transfer coefficients for vapors condensing on vertical tubes. Data were taken on film thicknesses and were correlated by means of an equation developed by dimensional analysis. Using the information on film thicknesses and data on heat transfer rates available in the literature, a method was developed which apparently has considerable merit.

Film Thickness

It seems quite probable that in industrial practice condensation occurs in the form of a film which may be in a viscous or turbulent state or a combination of these states depending upon the Reynolds number, $\left(\frac{\delta G}{\mu}\right)_b$. The film thickness δ is not easily evaluated so it is desirable to express $\frac{\delta G}{\mu}$ in other variables. The mass velocity G can be expressed as $\frac{W}{S}$ where

$$S = \frac{\pi[(D+2\delta)^2 - D^2]}{4} = \pi\delta(D+\delta)$$

Since δ is negligible in comparison to D for ordinary tubes the following is true

$$S = \pi\delta D \qquad (2)$$

$$G = \frac{0.318W}{\delta D}$$

$$\text{and } \frac{\delta G}{\mu} = 0.318 \left(\frac{W}{\mu D}\right) = \frac{C}{\mu} \qquad (3)$$

The heat transfer coefficient is a function of the condensate film thickness so it is therefore desirable to find a relation of δ with other variables. If it is assumed that the film thickness, δ, can be expressed in terms of the variables D, g, W, μ and ρ, a relation can be found by

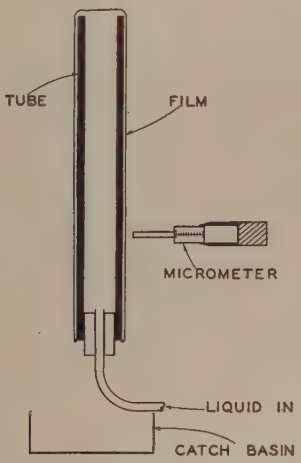

FIG. 1. Apparatus used to measure film thickness.

the use of dimensional analysis. It is apparent that there will be three dimensionless groups which can be written as:

$$\frac{\delta}{D}; \quad \frac{W}{\mu D} \text{ and } \delta\left(\frac{\rho^2 g}{\mu^2}\right)^{1/3}$$

Upon examining the problem further it appears that $\frac{\delta}{D}$ is of importance only when δ is not negligible in comparison with D. Thus, the final equation for ordinary cases is

$$\delta\left(\frac{\rho^2 g}{\mu^2}\right)^{1/3} = \chi\left(\frac{W}{\mu D}\right) \qquad (4)$$

which was found by experiment to be valid (Figure 2). The phenomenon of condensate flowing down a vertical tube was reproduced

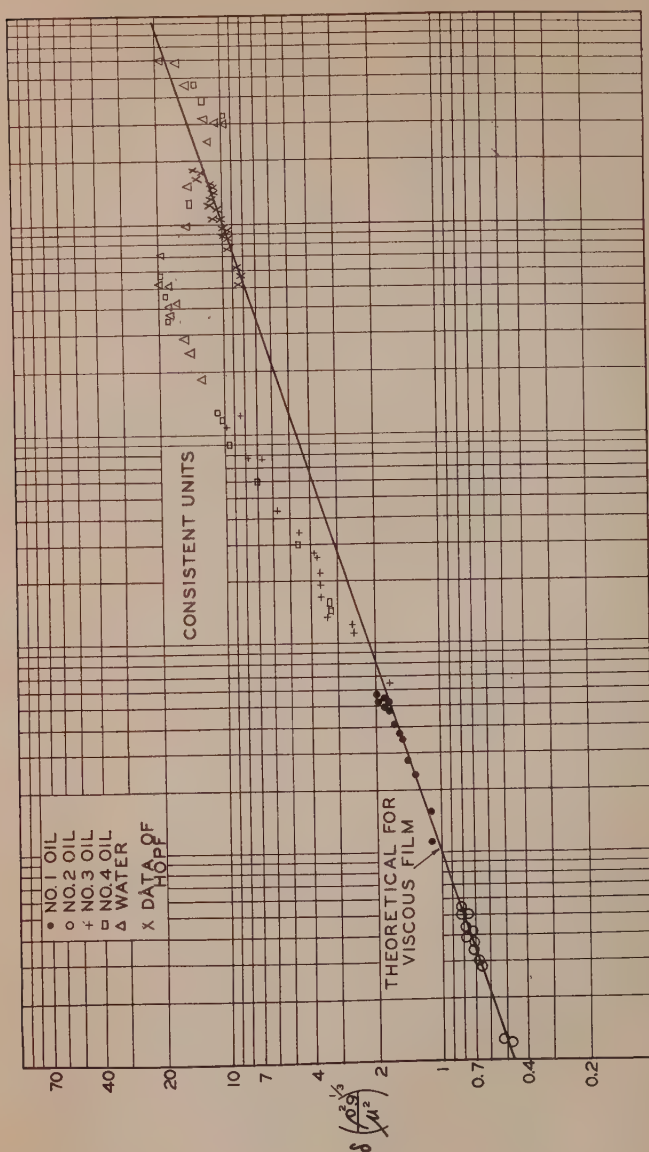

FIG. 2. Correlation of film thickness with the Reynolds number.

artificially with a very simple apparatus shown diagrammatically in Figure 1. The liquid under study was passed up through the vertical tube and down the outer wall. It was caught in a catch basin over a given period of time and weighed to 0.01 of a pound. The thickness of the liquid film on the outside of the tube was measured with a micrometer. The thickness was taken as that at which permanent contact was made between the liquid and micrometer. The film thickness measured was therefore the maximum and not the average. Where there is no disturbance on the film surface the maximum thickness will be equal to the average but such is not always the case. Results were correlated with equation 2 and are presented in Figure 2. Four hydrocarbon oils and water were studied under isothermal conditions. Their properties are given in Table I.

TABLE I

	Viscosity in Centipoises			Lb./ft.^{3}	Thermal Conductivity	
Liquid	100° F.	80° F.	70° F.	60° F.	100°	70°
Oil No. 1	11.3	17.6	23.5	54.9	$k = \frac{0.0677\ [1-0.0003(t-32)]}{\text{sp.g.}60°/60°}$	
Oil No. 2	23.6	49.0	75.0	55.8	"	"
Oil No. 3	1.15	1.95	2.80	51.2	"	"
Oil No. 4	0.49	0.56	0.62	46.2	"	"
Water	0.68	0.86	0.98	62.3	0.36	0.34
	600°F.	400° F.	200° F	400° F.		
Diphenyl	0.24	0.39	1.15	55.2	$k = 0.0035\ c\rho\left(\frac{\rho}{M}\right)^{1/3}$	

When taking the data it was made certain that the film thickness was constant all around the tube and then all observations were made from one location of the micrometer. Observations were made at various points for each liquid varying from 1 foot to 2½ feet from the top of the tube but the thickness was not found to be a function of the height. The data are presented in Table II.

TABLE II

Experimental Liquid	W/3600	Tube Diameter Inches	Film Thickness in Inches	° F.	$\frac{W}{\mu D}$	$\delta\left(\frac{\rho^2 g}{\mu^2}\right)^{1/3}$	f
Oil No. 1	0.00603	1.00	0.030	73	5.13	1.96	5.35
"	0.00325	"	0.022	"	2.77	1.43	7.25
"	0.00433	"	0.023	"	3.68	1.50	4.67
"	0.00483	"	0.025	"	4.11	1.63	4.81
"	0.00575	"	0.028	"	4.90	1.82	4.78
"	0.00565	"	0.027	"	4.80	1.76	4.43
"	0.00645	"	0.029	"	5.50	1.89	4.21
"	0.00616	"	0.027	"	5.25	1.76	3.72
"	0.00650	"	0.029	"	5.43	1.89	4.14
"	0.00672	"	0.030	"	5.72	1.96	4.30
"	0.00133	"	0.017	"	1.13	1.11	20.0
"	0.00183	"	0.018	"	1.56	1.17	12.5
"	0.00275	"	0.020	"	2.34	1.31	7.60
"	0.00412	"	0.023	"	3.50	1.50	5.20
Oil No. 2	0.00230	"	0.030	68	0.502	0.79	39.6
"	0.00228	"	0.030	"	0.497	0.79	40.5
"	0.00056	"	0.019	"	0.123	0.50	169
"	0.00058	"	0.020	"	0.127	.053	183
"	0.00128	"	0.025	"	0.279	0.66	74.2
"	0.00131	"	0.025	"	0.286	0.66	71
"	0.00167	"	0.027	"	0.364	0.72	55
"	0.00158	"	0.027	"	0.345	0.72	61.5
"	0.00192	"	0.028	"	0.419	0.74	46.5
"	0.00194	"	0.028	"	0.423	0.74	45.5
"	0.00204	"	0.029	"	0.445	0.77	45.6
"	0.00208	"	0.029	"	0.455	0.77	44
"	0.00221	"	0.029	"	0.482	0.77	39
"	0.00177	"	0.0293	"	0.387	0.78	62.7
"	0.00229	"	0.0295	"	0.500	0.78	38.3
Oil No. 3	0.00128	"	0.010	80	11.4	2.98	4.02
"	0.00605	"	0.019	"	53.0	5.66	1.23
"	0.00222	"	0.012	"	19.8	3.58	2.32
"	0.00383	"	0.015	"	34.1	4.47	1.52
"	0.00884	"	0.026	"	78.6	7.75	1.49
"	0.00100	"	0.007	"	6.4	1.67	2.28
"	0.00192	"	0.009	"	12.3	2.15	1.31
"	0.00260	"	0.015	"	16.6	3.58	3.30
"	0.00423	"	0.016	"	27.0	3.83	1.52
"	0.00208	"	0.014	"	13.3	3.35	4.20
"	0.00333	"	0.015	"	21.3	3.58	2.01
"	0.00408	"	0.019	"	26.1	4.55	2.73
"	0.0119	"	0.028	"	76.0	6.69	1.03
"	0.0175	"	0.041	"	112.0	9.75	1.49
"	0.0193	"	0.035	"	123.0	8.33	0.76
Oil No. 4	0.000433	0.85	0.005	76	15.6	3.20	2.57
"	0.00039	"	0.005	"	14.2	3.20	3.17
"	0.00133	"	0.007	"	30.0	4.47	1.91
"	0.00167	"	0.011	"	60.2	7.02	1.84

TABLE II—(*Continued*)

Experimental Liquid	W/3600	Tube Diameter Inches	Film Thickness in Inches	°F.	$\frac{W}{\mu D}$	$\delta\left(\frac{\rho^2 g}{\mu^2}\right)^{1/3}$	f
Oil No. 4 *Con't.*	0.0025	0.85	0.015	76	91.0	9.56	2.08
"	0.00333	"	0.016	"	121.0	10.23	1.42
"	0.0035	"	0.017	"	127	10.80	1.54
"	0.0096	"	0.014	"	347	18.30	0.115
"	0.0347	"	0.022	"	1255	14.10	0.034
"	0.1000	"	0.015	"	3620	9.57	0.0013
"	0.1070	"	0.019	"	3880	12.07	0.0023
"	0.1280	"	0.021	"	4630	13.30	0.0022
Water	0.0079	"	0.022	74	185	12.57	1.20
"	0.0105	"	0.024	"	245	13.73	0.88
"	0.0124	"	0.026	"	288	14.80	0.82
"	0.0176	"	0.030	"	412	17.17	0.61
"	0.0218	"	0.031	"	510	17.65	0.44
"	0.0321	"	0.034	72	708	19.15	0.27
"	0.0450	"	0.026	"	992	14.65	0.061
"	0.0695	"	0.025	71	1510	14.10	0.023
"	0.1125	"	0.020	"	2440	11.23	0.0044
"	0.1390	"	0.0170	"	3020	9.57	0.0018
Water	0.215	"	0.025	"	4670	14.07	0.0024
"	0.275	"	0.028	"	5970	15.65	0.0021
"	0.288	"	0.033	"	6250	18.70	0.0031
"	0.144	"	0.018	"	3120	10.15	0.0020
"	0.152	"	0.021	"	3300	11.80	0.0028
"	0.0234	"	0.030	"	507	16.70	0.35
"	0.0212	"	0.031	"	469	17.30	0.47

It is of interest to compare the observed results with the theoretical equation for a liquid flowing down a vertical wall in straight line motion. In Nusselt's derivation of equation (1) he showed that

$$u_m = \frac{\rho \delta^2 g}{3\mu} \tag{5}$$

by definition

$$u_m = \frac{W}{S\rho}$$

where

$$S = \pi D \delta$$

or

$$u_m = \frac{W}{\pi D \delta \rho} = \frac{\rho \delta^2 g}{3\mu}$$

and

$$\delta \left(\frac{\rho^2 g}{\mu^2}\right)^{1/3} = 0.984 \left(\frac{W}{\mu D}\right)^{1/3} \qquad (6)$$

It is seen (Figure 2) that the theoretical equation (6) is identical with the observed results up to $\frac{W}{\mu D} = 5$. Above this value ripples formed on the film surface and the measurements of maximum film thickness were no longer the same as average thicknesses. Were it not for data presented by Hopf [3] the theoretical equation might be questionable above $\frac{W}{\mu D} = 5$. His data however show excellent agreement with the theoretical curve up to about $\frac{W}{\mu D} = 1800$ (Figure 2).

In order to determine the value of $\frac{W}{\mu D}$ where the viscous condition breaks down into turbulence, it is convenient to plot the friction factor, f against $\frac{W}{\mu D}$ or $\frac{C}{\mu}$. The friction factor appears in the Fanning equation (7).

$$\triangle P = \frac{fLu^2\rho}{2gm} = \frac{fLu^2\rho}{2g\delta} \qquad (7)$$

and

$$\triangle P = \frac{SL\rho}{S} = \rho L$$

therefore

$$f = \frac{2g\delta^3\rho^2}{C^2} \qquad (8)$$

The friction factors were computed from equation (8) and are presented in Figure 3 along with the theoretical equation

$$f = 6\left(\frac{mu\rho}{\mu}\right)^{-1} = 6\left(\frac{C}{\mu}\right)^{-1} \qquad (9)$$

which is valid for liquids flowing in a straight line motion down vertical walls. The data show good agreement with the theory up to about $\frac{C}{\mu} = 2$. At this point the ripples cause a difference in maxi-

mum and average film thicknesses so generally higher results were obtained above this value. It is not possible to determine the critical value of $\frac{C}{\mu}$ from the data.

More exact data are necessary and there are at least two methods which might be used with considerably more success than that used

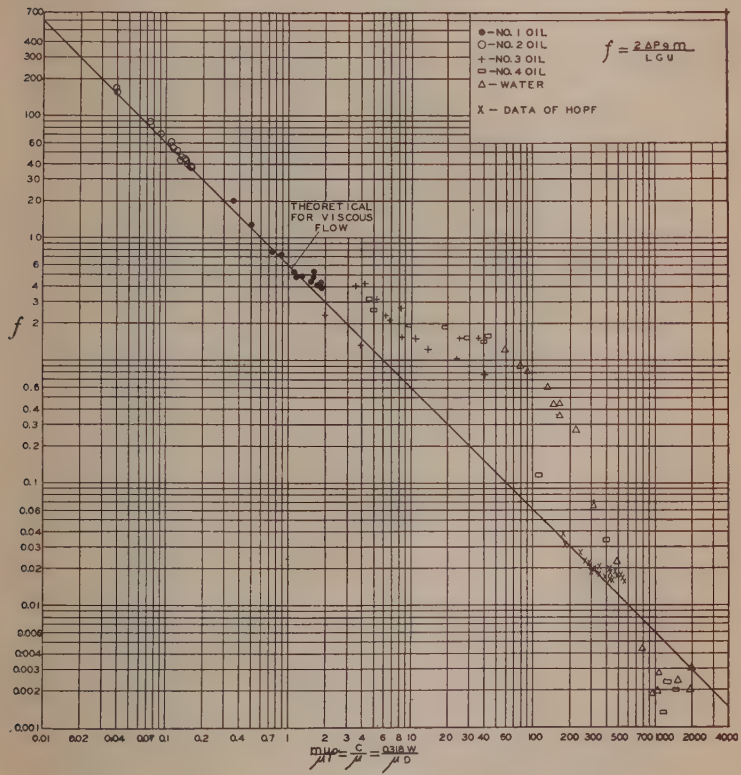

FIG. 3. Variation of friction factor with Reynolds number.

by the author. The first employs a photo-electric cell. A light is directed on a group of lenses which centralize the light rays into a fine beam. The beam is directed through the condenser tube and condensate film and finally on the photo-electric cell. The current produced in the photo-electric cell circuit is measured and by use

of a calibration curve the film thickness is obtained. The liquid must have considerable color for this method to be used with success. The second method makes use of an interferometer, one beam of light passing through the air and the other through the tube and liquid film. The band widths are measured and after calibration of the apparatus the actual thickness can be determined.

Correlation of Heat Transfer Data

Since observed film thicknesses are found to check the theoretical over a range of $\frac{W}{\mu D}$ up to about 1800 (Figures 2 and 3) it seems certain that the liquid is in viscous motion in this range. As this is the most important assumption made in the derivation of the Nusselt equation for condensation of pure vapor, this correlation can be considered additional support for that equation in the viscous range.

Since the condition of flow in the film and also the coefficient of heat transfer are a function of $\frac{W}{\mu D}$ it is desirable to express Nusselt's equation (1) in terms of $\frac{W}{\mu D}$ or $\frac{C}{\mu}$.

$$h_m = 0.943 \left(\frac{k^3 \rho^2 \lambda g}{\triangle t L \mu} \right)^{1/4} \qquad (1)$$

and

$$\lambda W_b = \pi D L h_m \triangle t \qquad (10)$$

therefore

$$h_m \left(\frac{\mu^2}{k^3 \rho^2 g} \right)^{1/3} = 1.35 \left(\frac{W}{\mu D} \right)_b^{-1/3} = 0.925 \left(\frac{C}{\mu} \right)_b^{1/3} \qquad (11)$$

Equation (11) can be considered valid up to at least $\left(\frac{W}{\mu D} \right)_b = 1800$. Above this value the condition of flow is not certain. Most industrial practice occurs above this value and according to data in the literature it is doubtful that Nusselt's equation applies.

The coordinates suggested by equation (11) were used to correlate the data available in the literature in the turbulent region. The data of Badger, Monrad and Diamond; Callendar and Nicolson; and Jordan were successfully correlated (Figure 4). One test was also available on a vertical tube condenser being used to condense a light hydrocarbon in commercial service. No tube temperatures were

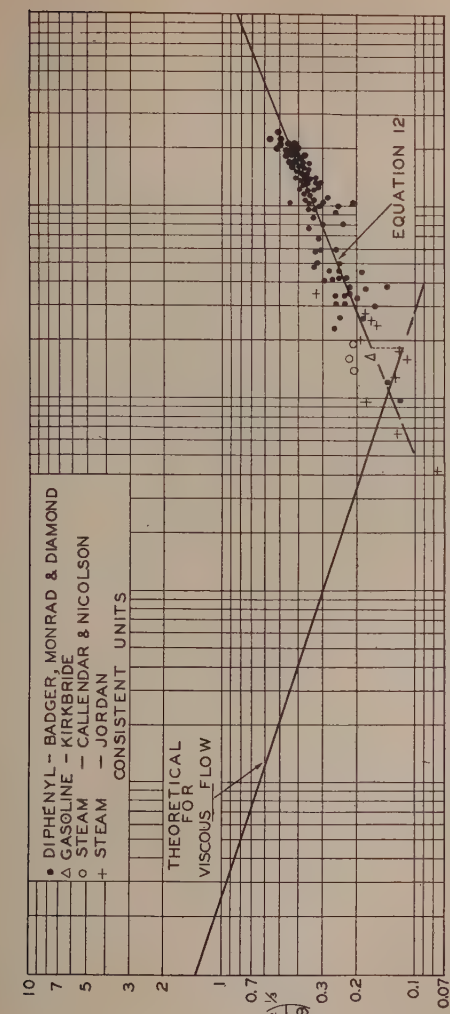

FIG. 4. The heat transfer coefficient is a function of the Reynolds number.

taken so the condensate film coefficient was computed from the overall coefficient and a predicted coefficient on the water side. The coefficient on the water side was calculated from a curve which is a combination of the Morris-Whitman and Lawrence-Sherwood curves as presented by Kirkbride.[5] The data are given in Table III.

TABLE III

TABLE I—DATA OF BADGER, MONRAD AND DIAMOND

Run	W/3600	$\left(\frac{W}{\mu D}\right)_b$	$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$
1	0.188	10,900	0.29
3	.165	10,200	0.21
4	.237	13,700	0.35
5	.201	12,500	0.32
6	.167	9,800	0.25
7	.287	17,700	0.40
11	.236	14,600	0.36
12	.247	15,200	0.36
13	.220	12,900	0.33
14	.241	14,800	0.39
15	.217	13,400	0.34
16	.212	13,200	0.32
17	.232	14,300	0.40
20	.243	14,800	0.37
21	.238	14,800	0.37
22	.218	13,600	0.34
23	.342	20,500	0.50
24	.387	23,900	0.52
25	.353	22,000	0.57
26	.277	17,100	0.38
27	.248	15,300	0.40
28	.275	17,000	0.43
29	.336	20,900	0.46
30	.330	20,400	0.50
31	.320	19,800	0.52
32	.295	18,200	0.39
33	.324	20,000	0.45
34	.335	20,700	0.43
35	.326	20,200	0.41
36	.308	18,900	0.41
37	.314	19,500	0.42
38	.312	19,300	0.42
39	.280	17,300	0.41
40	.248	15,300	0.37
41	.278	17,100	0.39
42	.268	16,600	0.43
43	.293	18,000	0.42
44	.232	14,300	0.41
45	.191	11,800	0.37
46	.182	11,200	0.36
47	.154	9,500	0.36
48	.138	8,600	0.34
49	.109	6,800	0.32
50	.283	17,500	0.45

TABLE III—*Continued*

TABLE II—DATA OF BADGER, MONRAD AND DIAMOND

Run	W/3600	$\left(\frac{W}{\mu D}\right)_b$	$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$
1	.211	12,000	.36
2	.246	13,900	.42
3	.109	7,900	.30
4	.114	8,000	.24
5	.148	10,400	.31
6	0.141	10,300	.30
7	.083	5,900	.26
8	.063	4,500	.25
10	.144	10,200	.46
11	.156	11,500	.37
12	.081	5,700	.33
13	.061	4,300	.25
14	.053	3,800	.22
15	.068	4,800	.34
16	.059	4,100	.27
17	.050	3,600	.22
18	.038	2,600	.19
19	.036	2,600	.25
20	.017	1,200	.14
21	.014	980	.12
22	.042	3,300	.20
23	.045	3,700	.18
24	.042	3,400	.26
25	.028	2,300	.27
26	0.040	3,300	.26
27	.037	3,100	.23
29	.212	13,200	.36
30	.183	11,200	.34
31	.149	9,500	.26
32	.103	7,700	.36
33	.070	5,000	.34
38	0.131	9,700	.33
39	.147	10,900	.38
42	.086	5,900	.32
43	.068	4,600	.28
44	.059	4,100	.30
45	.067	5,000	.25
48	0.141	11,300	.37
53	.042	3,400	.23
54	.052	4,100	.24
56	.047	4,500	.19
57	.031	3,000	.16
58	.039	3,800	.14

DATA OF CALLENDAR AND NICOLSON

1,900	0.208
1,600	0.218
1,400	0.212

TABLE III—*Continued*

DATA OF JORDAN

$\left(\frac{W}{\mu D}\right)_b$	$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$
410	0.078
660	0.125
950	0.180
1,300	0.129
1,600	0.110
1,700	0.117
1,700	0.329
2,000	0.193
2,400	0.159
2,500	0.172
2,700	0.186
3,500	0.340

DATA ON CONDENSER IN INDUSTRIAL SERVICE

Water Side							Condensate Side					
Q	Tube Diam. Ins.	Gal/ sec.	°F. t_1	°F. t_2	h	No. of Tubes	°F. Δt	h_c	A	Tube Diam.	$\left(\frac{W}{\mu D}\right)_b$	$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$
17,750,000	0.50	10.7	34	89.4	573	470	118	115	1800	0.625	1700	0.170

Over the range of the data the curve in Figure 4 has a slope of roughly 0.4 and can be expressed by equation (12).

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.0084\left(\frac{W}{\mu D}\right)_b^{0.4} \qquad (12)$$

Such a curve indicates that the most economical type condenser would be one which has rather long tubes. Considerable more data are needed, however, to determine the exact position of the curve in the turbulent region.

It is of interest that equation (12) can also be derived from the Nusselt equation (13).

$$\frac{h\delta}{k} = \text{a constant}\left(\frac{\delta G}{\mu}\right)^a\left(\frac{c\mu}{k}\right)^b \qquad (13)$$

which is valid for fluids flowing in turbulent motion, transferring heat by convection.

To use Figure 4 it is necessary to express the dimensionless groups

$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$ and $\left(\frac{W}{\mu D}\right)_b$ in consistent units. If the designer expresses D in inches, k in BTU/ft./°F/hr., W in lb./hr./tube, μ in centipoises, ρ in lb./ft.^{3} and disregards g he must multiply $h_m\left(\frac{\mu^2}{k^3\rho^2}\right)^{1/3}$ by 0.00241 and $\left(\frac{W}{\mu D}\right)_b$ by 4.96. These constants correct the respective groups expressed in such units to consistent units.

Acknowledgment

The author is indebted to Prof. W. H. McAdams of the Massachusetts Institute of Technology, Dr. Allan P. Colburn of the Du Pont Experimental Station and Prof. O. A. Hougen of the University of Wisconsin for their many helpful suggestions and criticisms. Thanks are also due Dr. R. L. Geddes of the Standard Oil Company (Ind.) for his helpful suggestions.

Nomenclature

Symbol	Meaning	Consistent English Units
a, b	Constants	—
A	Area	Sq. ft.
c	Heat Capacity	Btu/°F./lb.
C	Condensate/unit perimeter	Lb./ft./hr.
D	Diameter of tube	Ft.
f	Friction factor in Fanning Equation	—
g	Gravity	Ft./hr.^{2}
G	Mass velocity	Lb./ft.^{2}/hr.
h	Film coefficient	BTU/ft.^{2}/°F/hr.
k	Thermal conductivity	BTU/ft./°F/hr.
L	Tube length	Ft.
m	Hydraulic radius	Ft.
M	Molecular weight	—
Q	Duty	BTU/hr.
S	Cross sectional area of flow	Ft.^{2}
u	Linear velocity	Ft./hr.
W	Weight rate of condensation	Lb./hr./tube
δ	Film thickness	Ft.

ΔP	Pressure drop	Lb./ft.^{2}
Δt	Temperature difference through film	°F.
λ	Latent heat of condensation plus sensible heat of vapor	BTU/lb.
ρ	Density	Lb./ft.^{3}
μ	Viscosity	Lb./ft./hr.
χ	Represents a function.	

Subscripts	Meaning
c	Condensation
b	Bottom of tube
m	Average
w	Wall

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Discussion

(Summarized by T. H. Chilton, Chairman, Sub-Committee on Papers)

The first three papers on the program were presented as a group. In the absence of C. G. Kirkbride, his paper was presented by A. B. Newman. The discussion by A. P. Colburn was presented by T. H. Chilton, presiding. (See following written discussion.) W. L. Badger stated that he regarded the temperature of measurements of Hebbard as more accurate than those of Monrad which were used in the correlations by Kirkbride and by Colburn. He also believed that one effect not taken into account was the lengthwise flow of heat along copper condenser tubes.

Note on the Calculation of Condensation When a Portion of the Condensate Layer Is in Turbulent Motion* †

By A. P. Colburn

The paper by Kirkbride [5] attacks the problem of "film-forming" condensation by dimensional analysis, whereas it is felt that the complications of the case warrant an attempt at a more exact solution. Such a solution requires the determination of an expression for the condensation rate at each point down the length of the vertical condenser, and then an integration of the total condensation for the apparatus. Both steps are complicated for cases where the condensate layer becomes so thick near the lower end of the condenser that a portion of it flows in turbulent motion, but an attempt will be made to carry them out with several simplifying assumptions.

1. *Point condition values of heat transfer coefficient and condensation rate.*

For *viscous flow* of the condensate layer, the heat transfer coefficient at any point is equal to the quotient of the thermal conductivity, k, of the fluid divided by the layer thickness, m. This statement assumes that the amount of heat abstracted from or added to the condensate layer in passing the point is negligible compared to the heat conducted across the layer resulting from condensation. Nusselt [7] showed that since for viscous flow the thickness is expressed:

$$m = \left(\frac{3C\mu}{\rho^2 g}\right)^{1/3} \tag{1}$$

where C is the rate of flow of the liquid layer, expressed as weight per unit time and unit periphery, μ is the viscosity of the liquid, ρ the density, and g is the acceleration due to gravity, the heat transfer coefficient for viscous flow, h, at any given point on a vertical surface is equal to:

$$h = \left(\frac{k}{m}\right) = k\left(\frac{\rho^2 g}{3C\mu}\right)^{1/3} \tag{2}$$

Rearranging and multiplying both sides by $\mu^{2/3}$

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\mu}{3C}\right)^{1/3} \tag{2a}$$

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* Contribution No. 142 from the Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

† Presented as discussion at session on Principles of Chemical Engineering of the American Institute of Chemical Engineers, Roanoke, Va., meeting, December 13, 1933.

The differential rate of condensation, dC, over a differential length, dL, can be expressed:

$$dC = h \, \Delta t \, dL/\lambda \qquad (3)$$

where λ is the latent heat of vaporization and Δt is the temperature drop across the condensate layer.

Substituting the value of h from Equation 2a in Equation 3:

$$dC = \left(\frac{\Delta t \, dL}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{\mu}{3C}\right)^{1/3} \qquad (4)$$

For *turbulent flow* of the condensate layer the evaluation of the heat transfer coefficient is not so simple. In the absence of experimental data, it is possible to make use of an analogy with the case of heat transfer between a fluid and the walls of a rectangular conduit with a large aspect ratio, i.e., ratio of width to breadth. Cooper, Drew, and McAdams [4] show that the friction factor for turbulent flow in conduits can be used for flow of liquid layers. For heat transfer, the use of the analogous heat transfer factor is suggested even though such a procedure assumes that there is the same thermal resistance to the flow of all of the heat across the entire layer as there is for flow partially across, as is the case when heat flow results from a cooling of the flowing layer. The justification of this assumption is the fact that the main resistance to heat transfer for turbulent flow is across the viscous film next the surface.

The friction factor, f, for flow of liquid layers can be expressed:

$$\tfrac{1}{2} f = \frac{m^3\rho^2 g}{C^2} \qquad (5)$$

The heat transfer factor, j, is as follows [3]:

$$j = \left(\frac{h}{cG}\right)\left(\frac{c\mu}{k}\right)^{2/3} \qquad (6)$$

where G is the weight velocity expressed as weight rate per unit cross-sectional area, and c is the specific heat of the fluid.

Noting that $G = C/m$, and rearranging Equation 6, the following is obtained:

$$h = \frac{jcC}{m(c\mu/k)^{2/3}} \qquad (7)$$

For turbulent flow in conduits, it has been shown [3] that $\frac{1}{2} f = j$. Substituting this equality in Equation 5 and solving for m gives:

$$m = \left(\frac{jC^2}{\rho^2 g}\right)^{1/3} \tag{8}$$

Substituting Equation 8 in 7 and collecting variables into dimensionless groups:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{j}{2}\right)^{2/3}\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{1/3} \tag{9}$$

By analogy with turbulent flow in conduits,

$$j = a\left(\frac{4C}{\mu}\right)^{-n} \tag{10}$$

The constants a and n are tentatively taken as 0.027 and 0.2. Then:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.056\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{0.2} \tag{11}$$

The differential rate of condensation for turbulent flow becomes:

$$dC = 0.056\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{\triangle t\, dL}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{0.2} \tag{12}$$

2. *Integration of total condensation and determination of an average heat transfer coefficient.*

An exact general integration of Equations 4 and 12 over their respective ranges is difficult since the thermal properties and temperature difference usually vary along the length of the condenser. An exact integration of a particular problem can be carried out by a graphical method. Sufficient accuracy for most work can be achieved by taking the thermal properties at a mean temperature [3] and assuming a constant $\triangle t$, and the general integration will be carried out assuming them constant.

For *viscous region,* integration of Equation 4 gives:

$$C^{4/3} = \frac{4}{3}\left(\frac{\triangle tL}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{\mu}{3}\right)^{1/3} \tag{13}$$

Defining the mean heat transfer coefficient, h_m, over the length, L:

$$h_m = \frac{\lambda C}{\triangle t_m L} \tag{14}$$

and combining Equations 13 and 14 so as to eliminate L gives:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 1.47\left(\frac{4C}{\mu}\right)^{-1/3} \qquad (15)$$

Alternatively, combining Equations 13 and 14 so as to eliminate C gives the following form of the Nusselt equation:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.945\left[\left(\frac{\lambda\mu}{\triangle tL}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}\right]^{1/4} \qquad (16)$$

For the combined viscous and turbulent regions, integration of Equation 12 from a value of C_c at L_c to C_b at L_b gives:

$$\left(\frac{4C_b}{\mu}\right)^{0.8} - \left(\frac{4C_c}{\mu}\right)^{0.8} = 0.18\left(\frac{c\mu}{k}\right)^{1/3}\left[\left(\frac{\triangle tL_b}{\lambda\mu}\right) - \left(\frac{\triangle tL_c}{\lambda\mu}\right)\right]\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} \qquad (17)$$

The critical Reynolds number, C_c/μ, at which the type of flow changes from viscose to turbulent may vary over quite a range, as for flow in pipes. While the value is not known accurately, it will be tentatively assumed as follows:

$$4C_c/\mu = b = 1600 \qquad (18)$$

The value of $\frac{\triangle tL_c}{\lambda\mu}$ is obtained from Equation 13 when the above equality for $4C_c/\mu$ is substituted, giving:

$$\left(\frac{\triangle tL_c}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} = \frac{1}{4}\left(\frac{3b}{4}\right)^{4/3} = 3200 \qquad (19)$$

Substituting Equations 18 and 19 in 17 gives:

$$\left(\frac{4C_b}{\mu}\right)^{0.8} - 364 = 0.18\left(\frac{c\mu}{k}\right)^{1/3}\left[\left(\frac{\triangle tL_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 3200\right] \qquad (20)$$

Combining Equation 20 with 14 so as to eliminate L gives:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \frac{4C_b/\mu}{\frac{22}{(c\mu/k)^{1/3}}\left[\left(4C_b/\mu\right)^{0.8} - 364\right] + 12{,}800} \tag{21}$$

Alternatively combining Equation 20 with 14 so as to eliminate C:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\lambda\mu}{\triangle t L_b}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$$

$$\left[0.059\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{\triangle t L_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 190\left(\frac{c\mu}{k}\right)^{1/3} + 120\right]^{1.25} \tag{22}$$

Equations 21 and 22 can also be expressed generally by including the constants a and b rather than substituting numerical values, as follows:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} =$$

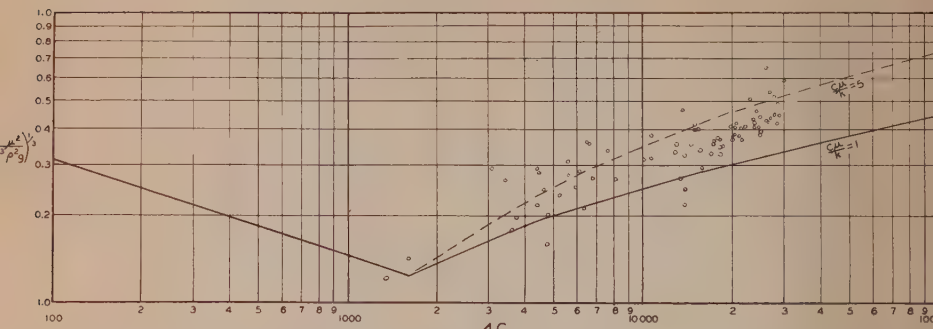
$$\frac{4C_b/\mu}{\left[\frac{1.25}{(a/2)^{2/3}(c\mu/k)^{1/3}}\right]\left[\left(4C_b/\mu\right)^{0.8} - b^{0.8}\right] + \left(\frac{3b}{4}\right)^{4/3}} \tag{23}$$

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\lambda\mu}{\triangle t L_b}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}\left[1.25\left(\frac{a}{2}\right)^{2/3}\right.$$

$$\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{\triangle t L_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 0.26\left(\frac{a}{2}\right)^{2/3}\left(\frac{c\mu}{k}\right)^{1/3}$$

$$\left.\left(\frac{3b}{4}\right)^{4/3} + \left(\frac{b}{4}\right)^{0.8}\right]^{1.25} \tag{24}$$

Figure 1 shows plots of Equations 15 and 21 and data on condensing diphenyl.[1] While the data scatter considerably, they show



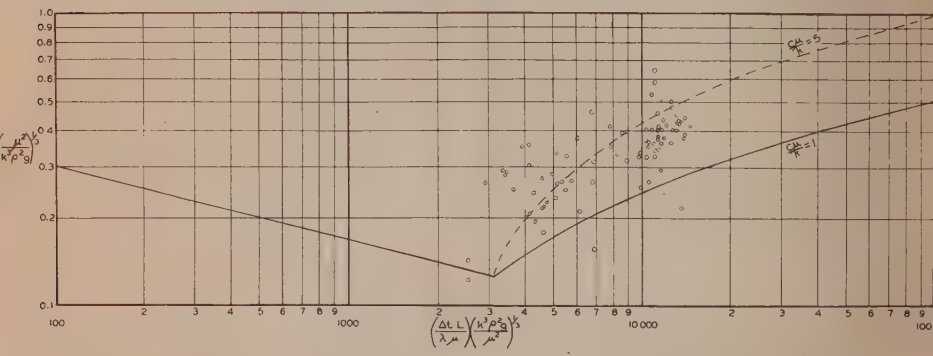


Figure 1. Condensation Film Coefficient. For use when number and diameter of tubes are assumed.

Figure 2. Condensation Film Coefficient. For use when length of tubes is assumed.

c = specific heat of condensate, P. c. u./lb.
C = condensate, lb./(hr.)(ft. perimeter of tubes), at bottom of condenser.
g = acceleration of gravity, 4.18×10^8 ft./(hr.)(hr.)
h = condensing vapor-film heat transfer coefficient, P. c. u./(hr.)(sq. ft.)(°C.).
k = thermal conductivity of condensate, P. c. u./(hr.)(sq. ft.)(°C./ft.).
L = length of tubes, ft.
Δt = temp. difference between vapor and tube surface, °C.
λ = latent heat of vaporization, P. c. u./lb.
μ = viscosity of condensate, lb./(hr.)(ft.).
ρ = density of condensate, lb./cu. ft.
(Any other set of self-consistent units may also be used.)

in general fair agreement with the predicted line for the turbulent region for a value of $c\mu/k = 5$. Inasmuch as the value of $c\mu/k$ of water is equal to 1.8 at 100° C. and 1.0 at 190° C., data on condensing steam (under film forming conditions rather than dropwise) would be expected to lie near the lower curve shown on the figure. This plot is convenient to use where the number and diameter of tubes can be conveniently assumed, thus fixing the value of $4C/\mu$ and the length is left variant. Alternatively, Figure 2 shows a plot of Equations 16 and 22 and the same data. This plot is convenient to use where the condenser length is fixed and the number and diameter of tubes is left variant. In the latter case it is necessary to estimate the mean temperature difference across the condensate layer, which may require cut-and-try calculations, based on the value for the overall logarithmic mean temperature difference. Since condenser lengths are more often fixed than the number and diameter of the tubes, Figure 2 will be preferred, nevertheless, by many engineers.

It should be noted that high vapor velocities in a downward direction will decrease the film thickness and increase the heat transfer coefficient thereby; they may also cause a transition from viscous to turbulent flow before the value of $4C/\mu$ becomes 1600. It is emphasized also that these equations do not hold under conditions causing "drop-forming" condensation,[6] but the evidence available indicates that "film-forming" condensation predominates with organic materials. It is, therefore, believed that the figures presented make possible a conservative determination of the heat transfer surface.

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STEAM FILM HEAT TRANSFER COEFFICIENTS FOR VERTICAL TUBES

By G. M. HEBBARD † and W. L. BADGER *

The larger part of the available data on heat transfer through films of condensed steam has been observed using horizontal tubes.[7] Only a few workers have investigated the films on vertical tubes. Some empirical relations have been established, but generally, the effort has been made to compare the data with some one of the theoretical equations that have been derived by W. Nusselt. Monrad and Badger [8] have reviewed the work on both types of tubes. For vertical tubes they found observed values of the steam film coefficients, ranging from 2000 to 3000 B. t. u.'s, that were from one-half to twice as large as corresponding values calculated by the theoretical equations. Several of their conclusions are quoted below.

"At present, all that may be said is that the fundamental theory of Nusselt is doubtless sound as is proved in the excellent correlation with the condensation of vapors on the outside of horizontal tubes—. The formulas developed for the case of vertical tubes are probably accurate for short tubes and low temperature differences, but are in general inaccurate for industrial operations, owing to the formation of drops."

In a recent article,[4] M. Jakob discusses his work and that of his collaborators, S. Erk and H. Eck, in comparison with the Nusselt theory for vertical tubes. He finds that for his experiments with steam passed slowly inside of a vertical tube, the data are in close agreement with the theory.[5] (The tube was 40 mm. in diameter and 1.20 m. long.) The results of other investigations, in which they have considered variables that are not included in the present work, also show that a theoretical correlation of the data is possible.

The shortest length of tube that would be employed in a forced circulation evaporator is about six feet and the usual length is from eight to ten feet. No published data can be found that concern vertical tubes of a length greater than four feet. Philipp [10] worked in

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this laboratory with tube lengths of four, six, and eight feet. In only one set of his runs was it possible to obtain consistent results. The individual coefficients obtained by him for steam were much higher than corresponding values which were calculated using the Nusselt theory.

Nusselt has considered the five following fundamental cases in his theory of the condensation of vapors.

(1) Vapor condensing on a smooth plane surface making the angle ϕ with the horizontal, assuming that the vapor is pure and saturated and relatively stationary with respect to the condensate.

(2) Vapor condensing on the outside of a horizontal tube under the above conditions.

(3) Vapor condensing on a surface as in (1) but with appreciable vapor velocity.

(4) Superheated vapor condensing on any surface.

(5) Impure vapor condensing on any surface.

This paper is not concerned with case (2). To some extent the factors in each of the other four cases may have an influence on the present problem. Case (1) is specific to this work, and will be made the basis for any theoretical consideration.

In order to simplify the mathematical treatment, Nusselt made the following assumptions.

a. The film of condensate is so thin that the temperature gradient through it is a straight line.

b. The heat is all carried to the metal surface by pure conduction in the direction perpendicular to the surface.

c. Physical properties of the condensate may be taken at the arithmetic mean film temperature.

d. The surface is relatively smooth and clean.

e. The film of condensate always moves in viscous motion.

f. The curvature of the film may be neglected.

g. The temperature of the solid surface is constant.

The mathematical relationship derived for case (1) follows: (The derivation, in English, is given by Monrad and Badger,[2] and Colburn and Hougen.[6])

$$h_s = 0.943 \frac{k^3 \rho^2 g r (\sin \phi)^{0.25}}{N \mu (t_s)}$$

g = gravitational constant, ft./h./hr. = 4.18×10^8
N = length of tube in feet = 11.969.
k = thermal conductivity of condensate, B.t.u./hr./sq·ft./°F./ft.
ρ = density of condensate, lbs./cu.ft.
r = latent heat of condensation, B.t.u./lb.
μ = viscosity of condensate, lb./ft./hr. = 2.42 × viscosity (in centipoises)
z = viscosity in centipoises
ϕ = angle between axis of tube and horizontal (for vertical tube, $\sin \phi = 1$)
Δt_s = temperature drop across film = °F.

All of the assumptions that have been made by Nusselt are reasonable, and certainly, the error involved in their use is not of sufficient magnitude to account for the discrepancies that exist between the experimental and theoretical observations. A lack of description of past operating conditions prohibits an unbiased effort to place the blame for the differences upon any one factor. With many investigators failing to profit by the errors noted by others, few researches may be relied upon for purposes of comparison.

The possibility exists that serious errors have been made in past determinations of tube-wall temperatures. This factor alone is sufficient to account for the unreliable character of much data. Moreover, if the degree of error that was possible were applied as a correction factor to the experimental data, the corrected values of the experimental coefficients would, in many cases, be in close agreement with the theoretical coefficients.

An accurate method for the measurement of tube-wall temperatures has been devised by Hebbard and Badger.[3] Their manner of attachment of thermocouples to the tubes permits a study of the films themselves: the occurrence and effect of turbulence in the steam film may be observed; and the results of varying the tube surface conditions noted.

The present investigation was conducted for the purpose of obtaining information bearing on the characteristics and heat transfer coefficients of steam films occurring on the tubes of vertical forced-circulation evaporators. The results, of course, have a fundamental application to the theory of heat transfer.

The Experimental Evaporator

The fundamental theory of Nusselt assumes conditions that may be employed as criteria in the design and operation of the experimental evaporator. These are: The steam used must be saturated and pure and must move past the evaporator tubes at a low velocity; the outer tube-surfaces must be smooth and clean and the normal flow of the steam condensate down the tubes must not be disturbed. The physical properties of the condensate are to be taken at the arithmetic film temperature.

When this work was initiated no equipment was available that fully met the requirements. A new apparatus was designed and assembled as shown in Figure 1. The steam jacket (1), constructed of four flanged sections of 6″ I.D. standard pipe, each 3 feet long, surrounded the 1″-11 gage copper experimental tube (2), which had a length of 12 feet exposed between the tube sheets. Distilled water for the boiler (18) was first passed through the preboiler (16) where it was boiled continuously to remove as much of the dissolved gases as possible before it was pumped to the boiler. The boiler was heated by steam from the University main. The steam to the jacket was passed first through a separator and then a super-heater (19) to remove all entrained moisture. The dry steam contained from 2-4°C. superheat. Condensate from the evaporator was used as feed liquor which was stored in tank (11). When the evaporator was operating under a vacuum, feed entered the system directly at the inlet to the circulating pump (8). At boiling points above atmospheric pressure, the feed was first piped to the feed pump (12). The liquor level in the vapor head (3) was maintained at a depth of approximately 4½ inches by manual control of the amount of feed added. The rate of circulation was measured by a sharp-edged thin-plate orifice (9) and controlled at the pump (8). Steam condensate and condenser condensate were collected and measured in the respective tanks (20) and (13).

Measuring and Control Devices

Thermocouples were used to measure the temperatures of: superheated steam, steam in the jacket, feed, circulating liquid at inlet to the tube, vapor in head (or circulating liquid at outlet to tube), liquid temperatures in tube (travelling couple), and the tube-wall. The exact points of the apparatus at which they were installed are shown

in Figure 1. The thermo-couples were read with a Type K-2 Leeds and Northrup potentiometer.

Briefly, the tube wall thermocouples (10 in number) were in-

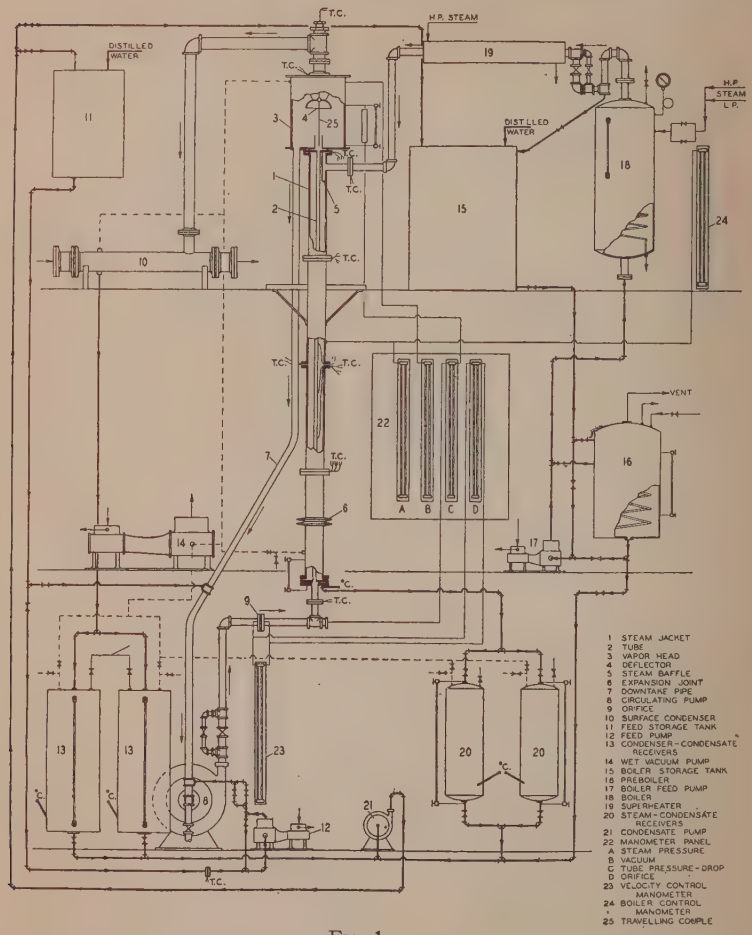

FIG. 1

stalled in the following manner. Each couple was inserted in the tube wall in a hole drilled through a chord of the wall. The leads were withdrawn under the surface to an annular groove at opposite

ends of the hole, carried in the groove to a point 180 degrees from the junction, and brought out from the wall together. The thermocouple junction was brought into metallic contact with the wall by means of solder which was inserted in a plug hole drilled in the wall at right angles to and intersecting the chord hole at the middle of the latter. Special Bakelite resin was used to insulate the leads and fill in each groove. The finished installations were free from the usual causes of heat conduction to the junction and did not disturb the steam film.

The tube couples were calibrated after the evaporator tube was placed in the steam jacket. The apparatus was slightly modified for this procedure by the installation of the following units: a mixing section consisting of a 6 x 6 inch flanged nipple on the top tube sheet in place of the vapor head; a double pipe heat exchanger in the inlet line between the circulating pump and the tube inlet; and an inlet mixing section of 6 inch pipe immediately before the tube inlet. The piping was so arranged that steam could be sent in parallel down the inside of the tube and jacket to the steam condensate tanks, and water could be circulated up the jacket and tube, the temperature of the latter being regulated by the heat exchanger. Water was used for the calibration in the range from 40 to 95°C. and steam from 100 to 130°C. When water was used the temperature gradient up the jacket was determined by means of thermocouples installed between each pair of flanges. This gradient was small (0.1-0.2°C.) because of the rapid rate of circulation; and since each tube couple was calibrated against the nearest reference couple, the limit of error in calibration was small (± 0.02°C.). After 150 hours of operation of the evaporator the tube couples were recalibrated with steam at atmospheric pressure. The calibration values for all tube couples checked the original values at this point within a limit of error 0.1°C.

Liquor temperatures inside the evaporator tube were measured with a thermocouple installed in a ¼ inch O.D. nickel tube of 16 feet length. The couple junction was placed at one end of the small tube, the leads being withdrawn through it to the opposite end. This small tube was inserted in the evaporator tube and was moved manually to any desired point. It was brought out of the evaporator through a stuffing box in the tee on the vapor head. The lead wires and the tube were held taut and carried upward by an arrangement of wires, pulleys, and counter weights located on the floor above the evaporator.

Mercury thermometers were used to measure the temperatures

of: steam condensate leaving the steam jacket, steam condensate in the steam condensate receivers and condensate in the condenser-condensate receivers.

The primary temperature-standard used for calibration of all thermocouples except the tube couple was a Leeds and Northrup platinum resistance thermometer. This thermometer was calibrated in the manner specified by the Bureau of Standards.[1] The equation derived from the calibration data for the thermometer was checked and found to be accurate within a limit of error of less than 0.01°C. over the range from 0-180°C. This thermometer was used to measure the temperature of a constant temperature bath in which the thermocouples were calibrated at intervals of 10°C. over the range from 30-150°C. The limit of error of the calibration was ± 0.01°C.

Open mercury manometers were installed to read the pressures in the boiler, steam jacket and vapor head. A mercury manometer was used to measure the pressure-drop through the evaporator.

Experimental Procedure

In this work the evaporator was operated at three different boiling points; 60, 80, and 100°C. Three overall temperature drops were employed with each boiling point, and four velocities of circulation, approximately 3, 5, 10, and 13 feet per second, were used with each combination of steam temperature and boiling point. A run consisted of a continuous experiment of 40 minutes duration, generally, and the data were so taken that each twenty minutes could be calculated separately.

During the run, a one inch depth of steam condensate was kept on the lower tube-sheet instead of allowing the condensate to drain freely to the tanks. This was necessary because of the relatively large surface area of the tanks, a fact that would have involved a correction factor of questionable accuracy for condensation of steam in the tanks. Noncondensible gases were removed from the jacket through a vent located about 10 inches above the lower tube-sheet, by continuous venting of a small quantity of steam.

All tube thermocouples were read three times during each run. The liquor temperatures were taken at the corresponding points with the travelling couple. The wall temperature at any couple position did not vary in any case more than ± 0.1°C. during a run. With small overall temperature drops (10°C.) the tube couples checked

consistently to within 0.02-0.04°C. The temperatures observed at the couples are tabulated in Table II. The average temperature drops across the steam film are also given in this table, as calculated by arithmetic and graphic averaging of the observed temperatures. The graphic average temperature differences were corrected for the small temperature gradients that existed between the actual outer surface of the tube and the average depth of immersion of the couples in the walls (0.001879 m.). The corrected results were employed in the calculation of the film coefficients.

All fundamental data have been tabulated in Table I. The values of the steam film coefficients (h_s) and apparent overall coefficients (U) have been calculated on the basis of an exposed outer tube-surface area of 0.2887 sq. m.

The heat-input was based directly on the amount of steam condensate collected per hour and included the super-heat, latent heat, and sensible heat extracted from this steam. The heat-output was calculated from the total amount of condenser condensate plus the sensible heat required to bring the feed to the boiling point. The amount of feed was assumed equal to the condensate collected. No allowance was made for entrainment and radiation losses were neglected.

Results

The factor limiting the accuracy of this work has been the possible error in the measurement of the volumes of the condensates. Large tanks were installed initially to provide capacity for a wide range of operating conditions. With small overall temperature differences the quantities of condensates collected were often so slight that an error in reading of 10-15% could have occurred.

A study of the heat balances indicated the occurrence of considerable entrainment in the vapor from the head. This factor expressed as the percentage excess of the heat-output over the heat-input did not show large errors, but it was considered unwise to use the data concerning the condenser condensate for any purpose other than just a semi-quantitative check of the steam condensate data. Two facts undoubtedly contribute to the cause of this entrainment. First, the deflector used was necessarily of a make-shift design. As it probably did not produce a uniform 'curtain' of liquid in the head, the vapor, rising from the tube at a high velocity, did not always pass through the curtain where the major portion of the entrained moisture

TABLE I—FUNDAMENTAL DATA

ENGLISH UNITS

Run No.	Satd. Steam ° F.	Satd. Vapor ° F.	Liquor Velocity Ft./Sec.	Overall ΔT ° F.	Wall Temp. (Correct) ° F.	Steam Film Δ T–°F. (Correct)	Mean Film Temp. ° F.	Heat Input Per Hr. B.T.U.'s	h_s (Obs.)	U app.
SEH 3A1	248.13	211.89	3.22	36.34	235.96	12.17	242.05	53.050	1405	470.0
3B1	248.09	211.66	3.22	36.43	235.92	12.17	242.01	52,990	1402	468.3
5A1	247.91	212.05	5.31	35.86	233.94	13.97	240.93	55,990	1264	502.7
5B1	247.91	212.00	5.37	35.91	233.96	13.95	240.94	57,310	1323	513.9
10A1	248.23	211.68	10.73	36.56	230.50	17.73	239.37	65,900	1197	580.4
10B1	248.09	211.91	10.73	36.18	230.38	17.71	239.24	66,300	1205	589.9
13A1	247.98	211.89	13.88	36.09	228.20	19.78	238.09	72,200	1175	644.0
13B1	247.96	212.13	13.83	36.84	228.16	19.80	238.06	71,950	1170	646.3
SEG 3A1	238.91	211.78	3.16	27.13	231.19	7.72	235.05	40,930	1706	485.8
3B1	238.91	211.78	3.16	27.13	230.77	8.14	234.84	41,600	1646	493.8
5A1	238.95	211.93	5.29	27.02	229.06	9.88	235.71	43,070	1403	513.2
5B1	238.95	212.00	5.29	26.95	229.06	9.88	235.71	44,160	1438	527.5
10A1	238.98	211.96	10.78	27.02	225.75	13.23	232.37	57,140	1390	680.8
10B1	238.89	211.96	10.75	26.93	225.63	13.27	232.27	53,310	1294	638.9
13A1	238.98	211.82	13.97	27.16	224.58	14.40	231.78	55,360	1238	656.2
13B1	239.02	211.91	13.94	27.11	224.62	14.40	231.82	56,380	1260	669.7
SEF 3A1	229.82	211.73	3.15	18.09	225.00	4.82	227.41	28,430	1898	505.9
3B1	229.82	211.69	3.16	18.13	225.01	4.81	227.43	25,920	1736	460.3
5A1	229.86	211.82	5.31	18.04	223.59	6.26	226.72	28,020	1440	500.1
5B1	229.96	211.82	5.31	18.14	223.72	6.25	226.85	37,440	1425	552.5
10A1	229.87	211.82	10.82	18.05	221.54	8.33	225.71	38,140	1473	680.0
10B1	229.87	211.91	10.82	17.96	221.54	8.33	225.71	38,100	1472	686.8
13A1	229.82	211.86	13.12*	17.96	221.14	8.68	225.48	38,430	1426	688.7
13B1	229.84	211.86	13.13*	17.98	221.16	8.68	225.50	38,530	1430	690.7
SCH 3A1	247.87	175.50	3.57	73.10	222.17	25.70	235.07	93,800	1175	413.1
3B1	247.96	175.50	3.63	72.47	224.11	23.85	236.04	86,520	1168	383.4
5A1	247.91	175.33	5.24	72.58	219.96	27.95	233.94	100,100	1153	441.4
5B1	247.91	175.24	5.31	72.67	219.40	28.51	233.66	100,100	1130	443.9
10A1	247.91	175.17	10.73	72.74	211.64	36.27	229.78	117,600	1044	520.4
10B1	247.84	175.10	10.68	72.74	211.37	36.47	229.61	124,600	1100	551.3
13A1	248.20	175.64	13.39	72.56	209.50	38.70	228.85	129,500	1086	573.1
13B1	248.32	175.64	13.44	72.68	209.12	39.20	228.72	128,200	1053	566.8
SCE 3A1	211.78	176.22	3.09	35.57	202.15	9.63	206.97	40,870	1366	369.9
3B1	211.82	176.43	3.12	35.39	202.05	9.77	206.94	42,940	1415	390.6
5A1	211.87	176.00	5.24	35.87	198.61	13.27	205.26	51,150	1241	459.0
5B1	212.04	176.22	5.22	35.82	198.95	13.09	205.50	49,110	1208	441.4
5A2	211.78	175.59	4.98*	36.20	197.22	14.56	204.50	52,150	1153	463.8
5B2	212.09	175.55	5.05*	36.54	196.68	15.41	204.39	54,210	1133	476.7
10A1	211.96	176.38	10.79	35.59	194.38	17.59	203.18	62,620	1146	563.6

	10B1	212.16	176.34	10.62	35.82	194.32	17.84	203.24	62,650	1131	563.0
	10A2	212.09	175.55	10.12*	36.54	194.25	17.84	203.17	61,550	1111	542.4
	10B2	212.05	175.23	10.25*	36.83	193.57	18.49	202.82	64,200	1118	561.1
	13A1	212.23	176.49	13.81	35.75	193.19	19.89	203.14	68,680	1161	618.4
	13B1	212.23	176.52	13.81	35.71	193.12	19.12	202.68	68,470	1153	617.3
	14A2	212.05	175.73	14.25*	36.32	192.92	19.13	202.49	66,930	1126	593.2
	14B2	212.16	175.37	14.35*	36.79	192.60	19.57	202.39	68,120	1121	592.0
SCD	3A1	194.04	174.83	3.11	19.21	188.94	4.49	191.19	26,610	1682	446.1
	3B1	194.00	174.92	3.05	19.08	188.92	4.62	191.23	23,190	1471	391.2
	5A1	193.91	174.88	5.35	19.03	187.21	6.70	190.56	29,670	1426	502.1
	5B1	194.00	174.92	5.37	19.08	187.38	6.72	190.74	28,800	1400	485.9
	10A1	193.77	174.42	10.78	19.35	184.69	9.07	189.23	36,440	1296	606.3
	10B1	193.91	174.83	10.78	19.03	186.78	8.93	191.25	35,550	1282	601.4
	13A1	193.91	174.49	13.81	19.42	183.79	9.94	188.76	37,690	1227	624.4
	13B1	193.77	174.78	13.92	19.01	183.87	9.90	188.82	37,700	1226	638.5
SAE	3A1	211.91	140.00	3.16	71.91	190.63	21.37	201.32	72,840	1097	326.0
	3B1	211.91	140.72	3.11	71.19	190.65	21.26	201.28	73,870	1119	334.1
	3C2	211.75	140.95	3.17	70.79	190.04	21.71	200.90	72,120	1070	327.9
	3C3	212.36	139.82	3.20	72.54	191.28	21.08	201.82	68,230	1042	302.9
	3C4	211.95	140.29	3.20	71.66	190.45	21.49	201.20	69,120	1035	310.5
	5A1	212.09	140.99	5.31	71.10	184.26	27.83	198.18	86,500	1001	391.6
	5B1	212.34	140.31	5.33	72.04	183.96	28.39	198.16	86,440	980.5	386.3
	5A2	212.14	140.05	5.24	72.09	184.28	27.86	198.21	80,870	934.5	361.2
	5B2	212.05	140.05	5.27	72.00	183.94	28.12	198.00	80,670	923.8	360.7
	10A1	212.14	140.59	10.78	71.55	175.28	36.86	193.71	108,300	945.3	487.1
	10B1	212.23	141.58	10.78	70.65	175.55	36.68	193.89	117,900	1035	537.3
	10A2	212.40	140.32	10.73	72.07	174.74	37.66	193.57	106,000	906.3	484.5
	10B2	212.63	140.81	10.73	71.82	175.12	37.51	193.88	107,900	925.8	483.5
	12A1	212.38	140.47	12.37*	71.91	173.95	38.43	193.17	113,800	953.5	509.5
	12B1	212.47	140.56	12.35*	71.91	174.04	38.43	193.26	113,800	953.5	509.5
SAD	3A1	194.00	140.49	3.15	53.51	177.04	16.96	185.52	55,540	1054	334.2
	3B1	194.00	140.81	3.15	53.19	177.12	16.88	185.56	54,490	1039	330.1
	5A1	194.04	139.89	5.37	54.14	171.32	22.72	182.68	72,640	1029	431.9
	5B1	193.91	140.13	5.38	53.98	171.82	22.09	182.87	71,900	1048	428.4
	10A1	194.05	140.27	10.78	53.78	165.24	28.82	179.65	92,290	1031	552.5
	10B1	194.00	140.14	10.80	53.86	164.86	29.14	179.43	82,200	908.3	491.5
	13B1	194.41	139.91	12.50*	54.50	163.92	30.49	179.17	83,440	881.0	493.6
SAC	3A1	176.31	139.82	3.16	36.49	166.23	10.08	171.27	38,580	1232	340.4
	3B1	176.27	140.45	3.16	35.82	166.12	10.15	171.20	40,580	1290	365.6
	5A1	176.32	140.27	5.37	36.05	162.23	14.09	169.28	45,870	1048	409.7
	5B1	176.13	140.58	5.38	35.55	162.07	14.05	169.10	45,900	1051	415.7
	10A1	176.00	140.61	10 84	35.39	157.46	18.54	166.73	58,260	1012	530.0
	10B1	175.60	140.52	10.84	35.44	157.35	18.61	166.66	57,290	991.0	520.5
	12A1	176.09	140.81	13.07	35.28	156.00	20.09	166.05	58,070	944.4	537.1
	12B1	176.22	140.14	12.75	36.07	156.02	20.20	166.12	59,880	932.9	522 4

* True velocity. Travelling couple not used.

Other velocities = 1.0625 × velocity corresponding to orifice manometer reading.

TABLE II.—WALL TEMPERATURES AT COUPLES AND STEAM FILM TEMPERATURE DIFFERENCES

WALL TEMPERATURES °C

(AT COUPLES)

Run No.	TUBE COUPLE NUMBER 1	2	3	4	6	7	8	9	10	Average ΔT, (Arith.)	(Graph.)
SEH 3A1	110.37	111.82	112.67	113.43	113.98	113.45	112.93	113.73	114.53	7.08	6.93
3B1	110.73	111.96	112.62	113.43	113.84	113.40	112.88	113.61	114.44	7.06	6.93
5A1	108.63	109.88	110.55	110.93	111.88	113.28	113.77	114.78	115.27	7.84	7.94
5B1	108.63	109.88	110.55	110.93	111.88	113.28	113.77	114.78	115.27	7.84	7.94
10A1	106.65	107.85	108.38	108.80	109.18	110.96	111.70	113.09	115.11	9.94	10.06
10B1	106.70	107.90	108.45	108.78	109.18	111.03	111.68	113.07	115.18	9.83	10.06
13A1	105.88	106.98	107.30	107.73	107.90	109.93	110.09	111.63	113.97	10.93	11.23
13B1	105.88	106.98	107.30	107.73	107.90	109.93	110.09	111.63	113.97	10.93	11.23
SEG 3A1	108.47	109.62	110.04	110.37	110.78	111.19	110.88	110.08	110.02	4.79	4.42
3B1	108.58	109.58	109.95	110.27	110.71	111.17	110.83	110.25	110.00	4.80	4.66
5A1	106.98	107.95	108.36	108.76	109.25	110.20	110.57	111.20	111.33	5.59	5.63
5B1	106.98	107.95	108.36	108.76	109.25	110.20	110.57	111.20	111.33	5.59	5.63
10A1	105.03	106.05	106.39	106.69	106.89	108.20	108.62	109.59	110.40	7.40	7.54
10B1	105.03	106.05	106.39	106.69	106.89	108.20	108.62	109.59	110.40	7.40	7.54
13A1	104.60	105.52	105.88	106.16	106.14	107.62	107.90	108.98	110.00	8.03	8.18
13B1	104.60	105.52	105.88	106.16	106.14	107.62	107.90	108.98	110.00	8.03	8.18
SEF 3A1	105.77	106.36	106.76	106.97	107.33	107.72	108.03	107.60	107.33	2.91	2.77
3B1	105.90	106.50	106.81	106.97	107.27	107.80	108.03	107.53	107.33	2.77	2.75
5A1	104.82	105.44	105.75	106.00	106.25	106.85	107.25	107.97	108.10	3.49	3.57
5B1	104.82	105.44	105.75	106.00	106.25	106.85	107.25	107.97	108.10	3.49	3.57
10A1	103.57	104.22	104.53	104.75	104.68	105.62	105.93	106.93	107.54	4.62	4.75
10B1	103.57	104.22	104.53	104.75	104.68	105.62	105.93	106.93	107.54	4.62	4.75
13A1	103.46	104.12	104.35	104.52	104.40	105.35	105.65	106.70	107.28	4.82	4.95
13B1	103.46	104.12	104.35	104.52	104.40	105.35	105.65	106.70	107.28	4.82	4.95
SCH 3A1	99.46	99.56	102.78	103.63	106.51	108.37	109.03	107.89	109.52	14.74	14.59
3B1	100.47	102.96	103.92	103.33	107.43	109.09	109.30	107.94	109.58	13.73	13.53
5A1	97.98	100.02	100.97	102.28	103.92	106.33	107.76	107.78	110.03	15.82	15.86
5B1	97.88	100.02	100.88	101.58	104.62	105.83	107.97	107.58	109.95	15.92	16.17
10A1	92.93	94.98	95.73	97.08	98.25	101.13	103.47	103.25	107.95	20.53	20.53
10B1	92.87	95.20	95.78	97.22	98.40	101.13	103.52	103.27	107.95	20.44	20.67
13A1	92.40	94.07	94.60	95.93	96.95	99.67	102.40	101.80	106.59	21.84	21.71
13B1	92.40	93.95	94.60	95.82	96.93	99.73	102.30	101.78	106.62	21.94	22.20
SCE 3A1	91.87	92.53	93.36	93.89	94.38	95.23	95.97	95.97	96.82	5.43	5.48
3B1	91.87	92.55	93.29	93.87	94.38	95.15	95.90	95.97	96.47	5.53	5.57
5A1	89.56	90.40	91.32	91.67	92.05	93.23	94.23	95.03	96.60	7.25	7.54
5B1	89.93	90.40	91.37	91.82	92.11	93.33	94.40	95.12	96.60	7.23	7.43
5A2	88.43	89.85	90.22	90.79	91.48	92.40	93.42	93.95	95.18	8.13	8.23
5B2	87.83	89.50	89.85	90.43	91.17	92.08	93.05	93.65	95.01	8.65	8.74
10A1	87.09	87.88	88.65	89.16	89.03	90.67	91.87	92.77	95.21	9.72	9.97

	10B1	87.09	87.93	88.60	89.16	88.97	90.65	91.82	92.85	95.23	9.83	10.11
	10A2	87.10	88.18	88.42	88.93	89.58	90.57	91.68	92.38	93.98	9.96	10.11
	10B2	86.10	87.78	88.10	88.68	89.32	90.28	91.08	91.83	93.65	10.38	10.48
	13A1	86.53	87.24	87.90	88.45	88.11	89.94	91.14	92.15	94.72	10.55	10.80
	13B1	86.48	87.26	87.83	88.50	88.16	89.94	91.16	92.17	94.72	10.56	10.84
	14A2	86.27	87.50	87.73	88.30	88.83	89.78	90.84	91.40	93.28	10.70	10.85
	14B2	86.10	87.22	87.48	88.05	88.63	89.57	90.73	91.36	93.27	10.93	11.09
SCD	3A1	85.77	86.45	86.70	86.83	87.00	82.33	87.75	88.19	88.35	2.87	2.92
	3B1	85.75	86.50	86.68	86.85	86.95	87.38	87.75	88.25	88.35	2.84	2.90
	5A1	84.63	85.27	85.55	85.95	85.77	86.38	86.86	87.38	87.82	3.77	3.82
	5B1	84.65	85.53	85.79	85.90	85.98	86.51	86.91	87.48	87.88	3.71	3.77
	10A1	83.44	84.15	84.35	84.48	84.22	85.07	85.52	86.25	86.83	5.05	5.16
	10B1	83.58	84.23	84.40	84.50	84.20	85.00	85.50	86.25	86.85	5.00	5.08
	13A1	83.00	83.71	83.84	84.00	83.61	84.55	85.10	85.77	86.41	5.51	5.64
	13B1	83.04	83.71	83.89	84.00	83.63	84.41	84.91	85.62	86.32	5.48	5.62
SAE	3A1	82.23	84.88	85.63	86.38	87.68	89.70	90.44	92.15	92.66	11.98	12.11
	3B1	82.49	84.88	85.90	86.70	87.78	89.75	90.42	92.10	92.66	11.87	12.05
	3B2	73.59	84.28	85.11	86.13	87.72	89.27	90.10	91.39	91.71	13.27	12.29
	3C3	83.26	85.03	86.28	87.13	88.52	90.17	91.01	91.83	90.86	11.97	11.93
	3C4	82.60	84.58	85.67	86.58	88.04	89.78	90.63	91.72	90.73	12.16	12.17
	5A1	72.50	79.91	81.22	82.24	83.63	86.48	87.00	89.67	92.11	16.08	15.74
	5B1	73.33	80.32	81.02	82.00	83.47	86.48	86.91	89.52	92.11	16.28	16.05
	5A2	72.36	80.18	81.27	82.60	84.37	86.51	87.59	89.00	90.30	16.28	15.74
	5B2	71.57	80.17	81.32	82.28	84.15	86.63	87.43	88.90	90.03	16.42	15.88
	10A1	67.72	75.18	76.23	77.00	77.95	81.07	81.40	85.05	89.13	21.11	20.83
	10B1	71.00	75.31	76.13	77.53	78.10	81.20	81.43	85.07	89.83	20.62	20.76
	10A2	67.07	74.88	75.78	77.01	78.38	81.63	82.15	83.98	87.58	21.50	21.27
	10B2	67.20	75.15	75.98	77.12	78.28	81.82	82.27	84.00	87.30	21.56	21.19
	12A1	67.00	74.93	75.45	76.41	76.69	80.43	80.63	84.34	88.56	21.94	21.72
	12B1	66.84	74.95	75.40	76.55	76.69	80.54	80.71	84.23	88.58	21.98	21.72
SAD	3A1	67.04	77.49	78.92	79.58	80.22	81.60	82.35	83.97	84.64	10.47	9.60
	3B1	67.04	77.54	78.73	79.50	80.22	81.55	82.35	83.95	84.73	10.49	9.56
	5A1	65.19	74.04	75.60	76.08	76.70	78.33	79.10	81.24	82.62	13.48	12.86
	5B1	64.08	74.30	75.49	76.10	76.75	78.35	79.95	81.08	92.62	13.43	12.50
	10A1	66.30	71.18	72.13	72.68	72.68	74.76	75.05	77.29	80.98	16.36	16.31
	10B1	63.52	71.03	72.03	72.58	72.55	74.58	74.93	77.23	79.56	16.88	16.46
	13B1	67.42	70.87	71.67	72.05	71.68	73.91	74.31	76.62	79.32	17.14	17.21
SAC	3A1	71.95	72.97	73.52	73.82	74.26	75.01	75.50	76.52	77.03	5.66	5.73
	3B1	71.78	72.85	73.52	73.80	74.21	75.03	75.52	76.57	77.05	5.66	5.77
	5A1	68.12	70.96	71.52	71.68	71.87	72.78	73.23	74.62	75.60	7.92	7.98
	5B1	68.33	70.88	71.47	71.62	71.72	72.73	73.23	74.62	75.53	7.83	7.96
	10A1	66.61	68.55	68.90	68.99	68.48	69.77	70.13	72.33	73.80	10.27	10.49
	10B1	65.95	68.31	68.79	68.94	68.65	69.90	70.18	72.43	73.92	10.31	10.53
	12A1	64.30	66.95	68.38	68.65	67.63	69.28	69.63	71.38	73.15	11.23	11.35
	12B1	64.49	67.20	68.40	68.58	67.89	69.33	69.61	71.28	73.00	11.26	11.41

was removed. Further, the vapor head was not specifically designed for the evaporator. It was neither of sufficient height to provide a satisfactory space above the deflector to allow for the natural separation of the entrained moisture by a decrease in vapor velocity; nor was it constructed in such a fashion that the level of liquid in it could be kept uniform without an excessive amount of control. In the case of the latter point, the effect was a change in the size of the curtain with each change in level and an increase or decrease in the vaporization with each variation in the rate of feed.

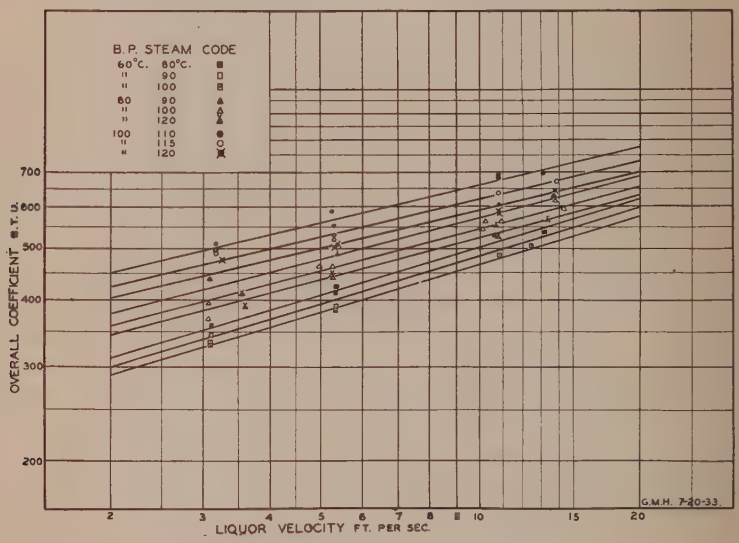

FIG. 2

Apparent overall coefficients of heat transfer, in general, do not have any specific bearing upon the values of the individual film coefficients that are obtained for the same experiments. For this reason, no detailed consideration of the former has been made. The fact that the overall coefficients may be correlated with themselves, however, is shown in Figure 2. In Figure 2, using log-log coordinates, the calculated overall coefficients (U) have been plotted against the corresponding velocities of circulation (V). Three groups of curves are evident, one group for each boiling point with a separate curve for each temperature drop used.

It may also be pointed out that the values of the coefficients are considerably lower than would be expected for a forced-circulation evaporator. The possible reason for this will be considered later.

The magnitude of the observed values of the steam-film coefficients is considerably less than any data of a similar investigation heretofore reported. On the basis of present theory five possible reasons may be advanced for this discrepancy. In accounting for them, the assumptions of Nusselt are recalled.

First, the tube used in this work is longer than any other previously employed in a study of steam films. Because of the greater possible thickness of the film on the lower part of the tube, the average rate of heat transfer will be less.

Second, when the evaporator tube was examined after completing the runs the outer surface was found to be covered with a thin but uniform layer of iron oxide that had been deposited over the usual "aged" surface of combined cupric oxide and sulfide. As indicated by Pridgeon and Badger [11] the presence of this oxide was sufficient to account for the low values of the coefficients. The oxide had evidently been carried over from the steam line and brought down into the jacket in a finely divided state. Absolutely no trace of oil was evident.

Third, if any noncondensible gas were present in the steam jacket low coefficients would have resulted. Othmer [9] observed that his coefficients for a horizontal tube were lowered by as much as half when 1% of air was present in the steam. Although the statement cannot be made definitely that the steam used in this work was absolutely free from air and other noncondensible gases, the use of distilled water for boiler feed and the operation of the preboiler furnish strong grounds for assuming that the steam was "practically" air-free. Further, there is no reason to assume that other workers have used absolutely pure steam. At least, they have never reported either special precautions in preparing the steam, or measurements of air content by either direct or indirect methods.

Fourth, the magnitude of the observed temperature drop through the steam films is greater than the average of the few published results. As previously stated, this fact would in itself account for the difference. Considerable data for liquor film coefficients, obtained by the use of wall temperatures measured under steam films, cannot be brought into an agreement of closer than 10% with data derived by other methods of wall temperature determination.

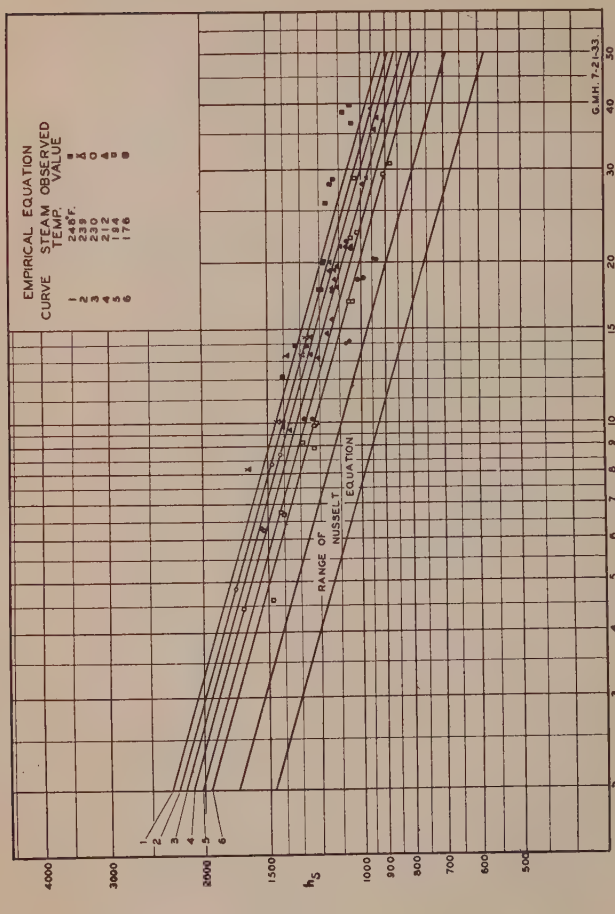
EMPIRICAL EQUATION
CURVE STEAM OBSERVED VALUE TEMP.
1 249°F. ■ ▲
2 239 ○
3 230 ○
4 212 ▲ ■
5 194 ■
6 176 ●
RANGE OF NUSSELT EQUATION
h_S
ΔT_S °F.
G.M.H. 7-21-33.

FIG. 3

Fifth, the occurrence of dropwise or combined dropwise and film-type condensation on the tubes during previous work might possibly account for their higher results. Coefficients have been obtained with dropwise condensation that were from 4 to 8 times the magnitude of those received for known film-type condensation.[12] Lack of actual information concerning this point for any investigation of the present scope prohibits more than a surmise of the effect of this factor. It is probable, however, that the surface of this tube would produce film-type condensation.

There is no doubt that the observed coefficients of this work are lower than those that would have been obtained if the layer of iron oxide had not been present. The layer was probably deposited on the tube during the calibration of the tube couples as the data indicated that surface conditions remained constant during the series of runs. Some method is essential whereby the outer tube-surface can be examined and kept clean during the experiments. But no worker has yet reported such care of the surface when the experimental tubes were equipped with thermocouples. These surface layers no doubt form quickly and check runs will not indicate their presence.

The answer to the question remains unsettled. More work must first be done of a nature that considers all of the factors concerned.

Correlation of Coefficients with Nusselt Equation

Values of the steam film coefficients were calculated for each run from the Nusselt equation (1). The difference between the observed and calculated coefficients for each case was then expressed as percentage of the experimental value. These percentages were found to vary within narrow limits (Table III). When an average percentage had been obtained the individual divergencies from this mean were observed to be within the limit of experimental error.

Reference to equation (1) will show that a relation involving the same variables, but with a different constant, can be used to express the experimental results.

Equation (1) was applied to this work in the following form:

$$h_s = 58.12 \left\{ k^3 \rho^2 r / z(\triangle t_s) \right\}^{0.25}$$

Values of h_s as calculated from the above equation are tabulated in Table III.

TABLE III—COMPARISON OF COEFFICIENTS

Run No.		h_s (Exp.)	h_s Nusselt	Deviation %	h_s (Calcd.)	Deviation %
SEH	3A1	1405	1021	27.3	1364	−2.9
	3B1	1402	1021	27.2	1364	−2.7
	5A1	1264	984	22.2	1314	+4.0
	5B1	1323	984	25.6	1315	−0.6
	10A1	1197	943	21.2	1260	+5.3
	10B1	1205	943	21.7	1260	+4.6
	13A1	1175	895	23.8	1195	+1.7
	13B1	1170	895	23.5	1195	+2.1
				24.06		+1.44
SEG	3A1	1706	1127	33.9	1505	−11.8
	3B1	1646	1112	32.2	1485	−9.8
	5A1	1403	1061	24.4	1417	+1.0
	5B1	1438	1061	26.2	1417	+1.5
	10A1	1390	979	29.5	1307	−6.0
	10B1	1294	977	24.5	1306	+0.9
	13A1	1238	956	22.8	1277	+3.1
	13B1	1260	956	24.1	1276	+1.3
				27.20		−2.35
SEF	3A1	1898	1247	....	1665	....
	3B1	1736	1247	28.2	1666	−4.0
	5A1	1440	1166	19.0	1557	+8.1
	5B1	1425	1166	18.2	1558	+9.3
	10A1	1473	1082	26.6	1445	−1.9
	10B1	1472	1082	26.5	1445	−1.8
	13A1	1426	1071	24.9	1430	+0.3
	13B1	1430	1071	25.1	1431	+0.0
				24.07		+1.43
SCH	3A1	1175	833	29.1	1112	−5.4
	3B1	1168	850	27.2	1136	−2.7
	5A1	1153	813	29.5	1086	−5.8
	5B1	1130	809	28.4	1081	−4.3
	10A1	1044	755	27.7	1008	−3.4
	10B1	1100	754	31.2	1007	−8.4
	13A1	1086	741	31.8	990	−8.8
	13B1	1053	738	29.9	986	−6.4
				29.60		−5.65
SCE	3A1	1336	1001	36.5	1336	−2.2
	3B1	1415	997	29.5	1331	−5.9
	5A1	1241	920	25.8	1229	−1.0
	5B1	1208	924	23.5	1234	+2.2
	5A2	1153	897	22.2	1198	+3.9
	5B2	1133	884	22.0	1181	+4.2
	10A1	1146	853	25.6	1140	−0.5
	10B1	1131	851	24.7	1136	+0.4
	10A2	1111	850	23.5	1136	+2.3
	10B2	1118	842	24.7	1125	+0.6

Run No.		h_s (Exp.)	h_s Nusselt	Deviation %	h_s (Calcd.)	Deviation %
SCE	13A1	1161	828	28.7	1105	−4 8
	13B1	1153	835	27.6	1115	−3.3
	14A2	1126	834	26.0	1114	−1.1
	14B2	1121	829	26.1	1108	−1.2
				26.17		−0.50
SCD	3A1	1682	1166	30.6	1557	−1.6
	3B1	1471	1158	21.3	1546	+5.1
	5A1	1426	1054	26.1	1408	−1.3
	5B1	1400	1054	24.6	1408	+0.6
	10A1	1296	973	24.9	1300	+0.3
	10B1	1282	983	23.3	1312	+2.3
	13A1	1227	952	22.2	1271	+3.6
	13B1	1226	951	22.4	1270	+3.6
				24.44		+1.57
SAE	3A1	1097	830	24.4	1109	−0.9
	3B1	1119	829	25.9	1108	−0.9
	3C2	1070	806	24.7	1076	+0.6
	3C3	1042	814	21.7	1087	+4.3
	3C4	1035	808	22.0	1079	+4.3
	5A1	1001	752	24.9	1004	+0.3
	5B1	981	748	23.8	999	+1.8
	5A2	935	752	19.6	1004	+7.5
	5B2	924	750	18.4	1001	+7.3
	10A1	945	693	26.7	926	+8.6
	10B1	1035	698	....	934	....
	10A2	906	689	24.0	920	+1.5
	10B2	926	691	25.4	922	−0.2
	12A1	954	685	28.2	915	−4.0
	12B1	954	684	28.2	914	−4.0
				24.13		+1.87
SAD	3A1	1054	826	21.6	1104	+4.7
	3B1	1039	826	20.5	1104	+6.2
	5A1	1029	761	26.0	1017	−1.1
	5B1	1048	767	26.8	1025	−2.2
	10A1	1031	711	31.0	949	−7.9
	10B1	908	710	21.8	948	+4.4
	13B1	881	702	20.3	938	+6.5
				24.00		+1.66
SAC	3A1	1239	912	26.4	1218	−1.7
	3B1	1290	910	29.4	1216	−5.7
	5A1	1048	836	20.2	1116	+6.5
	5B1	1051	834	20.6	1115	+6.1
	10A1	1012	773	23.6	1033	+2.0
	10B1	991	772	22.1	1031	+4.0
	12A1	944	761	19.4	1017	+7.7
	12B1	933	760	18.6	1015	+8.8
				22.54		+3.46

All % Deviations are based upon % of experimental (Exp.) values. Average % Deviation of h_s (Exp.) — h_s (Nusselt) = +25.13%.
Average % Deviation of h_s (Exp.) — h_s (Calcd.) = +0.33%.

Expressed as percentage the mean value of:

$$\frac{h_s \text{ (observed)} - h_s \text{ (Nusselt)}}{h_s \text{ (observed)}} = 25.13\% \text{ for all runs.}$$

Let E equal the constant of an empirical equation with the same variables as the Nusselt equation. When the Nusselt constant equals 58.12

$$E - 0.2513\ E = 58.12$$

$$\text{or } E = 58.12/0.7487 = 77.63 = \text{the new constant.}$$

The empirical equation is:

$$h_s = 77.63 \left\{ k^3 \rho^2 r/z(\triangle t_s) \right\}^{0.25}$$

When the coefficients were recalculated by this equation, in no case was the deviation of the calculated from the observed values over $\pm$ 5% for any one run; and the average deviation for all runs was +0.33%.

A correlation of the results of the present investigation with the theoretical equation is evidently possible. The question arises whether or not such a correlation is specific to the present apparatus.

A current project in this laboratory has made use of the same method of wall temperature measurement employed here in an investigation of the steam and liquor film coefficients for an eight-tube forced circulation evaporator that was concentrating sucrose solutions. Six thermocouples were installed on an 8 ft. x 1 in. 11 gage, copper tube. The remaining tubes were 8 ft. x 7/8 in. 16 gage, copper.

The data given in Table IV were taken from the records of the above project. Only a few representative runs that covered the range of operation have been examined. Calculation of Nusselt coefficients for these runs show the results given in Table V.

If an empirical constant for this data was applied to the theoretical equation, as before, the calculated values of the individual coefficients would evidently not diverge from the observed values by an amount greater than the possible experimental error.

The data reported in other parallel work are not sufficiently complete to warrant a similar treatment. It is assumed, however, that a corresponding correlation might have been obtained.

TABLE IV.—EIGHT FOOT VERTICAL-TUBE F. C. EVAPORATOR, OPERATING DATA

RUN	% Sucrose	Satd. Steam ° F.	Super-heat ° F.	Liquor Temp. ° F.	Liquor Velocity Ft./Sec.	t_s ° F.	h_s (Exp.) B.T.U.
BP 140	48.6	252.9	4.7	218.3	7	10.9	1955
240	48.5	252.9	5.3	217.7	10	12.8	1855
340	48.7	252.8	2.1	216.7	14	16.4	1640
440	48.5	252.8	0.9	215.9	18	18.2	1535
AL 140	19.3	214.2	0.5	178.1	7	11.2	1920
240	19.2	214.6	0.0	177.1	10	19.1	1510
340	19.2	214.0	0.0	176.5	14	22.4	1370
442	19.0	214.0	51.2	176.0	18	22.9	1405
AK 130	19.1	190.6	13.3	164.8	7	11.2	1630
230	19.3	190.6	3.6	163.9	10	13.4	1525
330	19.1	189.4	22.1	163.0	14	14.6	1460
430	19.1	189.4	17.4	163.4	18	16.6	1390

TABLE V.—COEFFICIENTS CALCULATED FROM DATA IN TABLE IV.

RUN	h_s (observed)	h_s (Nusselt)	Percent Difference	Average Percent
BP 140	1955	1143	+41.5	
240	1855	1110	40.0	
340	1640	1027	37.4	
440	1535	1001	34.8	+38.4
AL 140	1920	1070	44.3	
240	1510	929	38.5	
340	1370	889	35.0	
442	1405	882	37.2	+38.8
AK 130	1630	1015	37.8	
230	1525	968	36.6	
330	1460	942	35.5	
430	1390	909	34.6	+36.1
			NET AVERAGE	+37.77

WALL TEMPERATURES AND TURBULENCE

As previously stated, it was felt that information concerning the wall temperatures of the tube would explain much concerning the steam film. To this end, in Figure IV the observed wall temperatures for the last half of each run were plotted against respective positions

on the tube. A curve was drawn through the plotted data of each run. These curves were grouped according to the temperature drops used.

A definite and orderly form was immediately noticeable in each group of curves. The wall temperature decreased with distance from the upper tube-sheet. As the liquor velocity was increased the temperatures were lowered in proportion at all points except for an irregularity displayed in several cases at the upper part of the wall, when a 3 foot velocity was used. The latter divergences from the general form of the curves are reproducible in each case, but as a discussion of them must consider a study of conditions inside of the tube they are left for another paper.

Jakob and Erk,[6] working with a vertical tube of 0.466 m. length, found that at high temperature differences the tube temperature first decreased, then increased at some point down the tube, and finally decreased slightly. A similar observation was made with the tube of the eight foot evaporator previously mentioned, except that the last temperature decrease was usually quite large and brought the wall temperature at the bottom to a point several degrees below that of the top.

Evidently the occurrence of uniform and cyclic variations in wall temperatures was not previously noted by other investigators, either because of the length of tube used or because of the inadequacy of the method of wall temperature measurement.

Monrad and Badger[8] stated that "with increasing turbulence due to larger temperature drops, the coefficients would deviate more and more from the theory until the amount of heat going through the region covered by a purely viscous film is negligible. From this point on the deviation might be expected to be about constant, or at least not change as quickly. This statement is equivalent to saying, that above a given temperature drop, the turbulent portion of the film controls the rate of heat transfer. Their conclusions were based upon observations made with condensing diphenyl vapor. In the present work with steam no such behavior was noticed. The deviations from the Nusselt theory was practically constant; if anything, a smaller deviation was observed with larger temperature drops. The degree of turbulence caused by the flow of steam condensate is undoubtedly less than would be encountered with diphenyl as the amount of steam condensed on a given tube would be much less than the amount of diphenyl that would be required to supply an equivalent quantity of latent heat.

This investigation has proven, that for steam condensing on a twelve-foot vertical tube, turbulence in the film does not control the rate of heat transfer. The application of a theoretical equation to the data is possible, but turbulence appeared to effect the film in such a fashion that a constant deviation must be considered from the equation as derived for a purely viscous film.

The conditions under which turbulence may be expected to begin cannot be stated from the results of this work. A more thorough examination of conditions with tubes of different lengths and small temperature drops is necessary. The practical importance of a study of turbulence in steam films dwindles, however, if a proper verification is made of the data of this work.

Summary

1. Steam film coefficients of heat transfer, determined for a 1-in. O.D. vertical tube over a wide range of operating conditions (84 runs) with practically air-free steam, do not check the Nusselt equation. If a constant factor of 1.2513 is now applied to this equation, all runs within the limit of accuracy of the work for the greatest individual deviation (approx. $\pm 5\%$), and within $+0.33\%$ for the average of all runs. A similar relation is shown to be possible with the data of a parallel investigation.

2. The cause of the deviation of the present coefficients from other results is probably due partly to a layer of iron oxide on the evaporator tube, partly to the use of a longer tube than was heretofore employed, and partly to less accurate methods for wall temperature measurement used in all previous work.

Literature Cited

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Discussion

H. McCormick (written) : The paper on Steam Film Heat Transfer Coefficients for Vertical Tubes presented by G. M. Hebbard and W. L. Badger at the Roanoke meeting of the Institute attempts to correlate the experimental and the calculated steam film coefficients for a vertical tube.

It is believed that the method outlined in this paper, the correlation of the experimental steam film coefficient with the calculated steam film coefficient by multiplying the experimental coefficient by a constant factor, is applicable solely within operating conditions such as described in this paper and with equipment such as is described.

Some experimental evidence is available to support this opinion.

The authors recommend the correlation of experimental and calculated steam film coefficients by applying the constant factor .2513 to the Nusselt equation.

The use of this factor satisfactorily correlated the data obtained by the authors on the 12′ x 1″ 11 gauge copper tube which was used in their investigations while measuring the transfer between steam and boiling water. The authors, however, quote in table 4 results obtained on the operation of a vertical 8′ x 1″ 11 gauge copper tube when the transfer is between steam and boiling surcrose solution.

The factor found to apply under these conditions is .377 to correlate the steam film coefficient as calculated from the Nusselt equation with the steam film coefficients as found experimentally.

Stating these results in a slightly different manner, the steam film coefficients as calculated from Nusselt's equation under one set of operating conditions deviate from the experimental steam film coefficients by 25.13%; with other operating conditions, the authors find that this deviation amounts to 37.77%.

A paper presented before the Detroit meeting of the Institute and published in Volume 24 of the Institute Transactions dealing with "Heat Transmission in an Experimental Inclined Tube Evaporator," the authors being C. M. Linden and G. H. Montillon, presents seemingly reliable data from which it is possible to calculate steam film coefficients by the Nusselt equation.

Certain of their experimental runs selected at random from their tabulated data, give experimental steam film coefficients deviating from the calculated Nusselt steam film coefficient by percentages ranging from 64.5 to 75.

There is also available considerable experimental data on a 6′6″ x 1″ extra heavy copper tube operated in the laboratories of Armour Institute of Technology. The steam film coefficients obtained in this work deviate by from 40% to 85% from the steam film coefficients as calculated by the Nusselt equation. The opinion is, therefore, expressed that it is impossible to correlate experimental

steam film coefficients with steam film coefficients calculated by the Nusselt equation by the use of such a simple expedient as multiplying the steam film coefficients calculated from the Nusselt equation by some constant factor.

THE DROP-WISE CONDENSATION OF STEAM †

By W. M. NAGLE * and T. B. DREW *

Anyone who has seen mist forming on a mirror knows that water vapor may condense in droplets on a cold surface. The chemist who has conducted distillations in glass has seen the clear, though sometimes rippled, film of condensate wetting the interior of his condenser; and, when condensing steam in an imperfectly cleaned tube, he has doubtless observed dry areas wherein drops form, coalesce, and slide into an irregular rivulet flowing down the tube. These phenomena are not new. Nevertheless, their full significance seems not to have been appreciated. Not until 1930, when Schmidt, Schurig and Sellschopp [16] published the results of their brilliant researches, was it definitely known that there were marked differences between the heat transfer coefficients for the two modes of condensation.

The present investigation was undertaken to explain observations made during a study of the water-side coefficient of heat transfer in a falling-film condenser. During twelve hours of continuous operation the capacity of the condenser was repeatedly found to increase about 60% from an initial value of approximately 90 lbs. of steam/(hr.)(sq.ft.) to 145 lbs. of steam/(hr.)(sq.ft.), although there was no corresponding change in the operating conditions imposed upon the apparatus. By careful study the cause of this behavior was proved to be an increase of the steam-side coefficient of heat transmission, and the results of Schmidt, Schurig, and Sellschopp indicated that the change might be associated with a shift from film to drop-wise condensation.

The very nature of drop-wise condensation, occasioned as it is by the non-wettability of the cooling surface, indicates the necessity of an extended excursion into the field of surface chemistry. Whatever the magnitudes of the heat transfer coefficients, a knowledge of these quantities is useless unless it is known how to maintain and control

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† Abstracted from a portion of a thesis submitted to the Faculty of the Massachusetts Institute of Technology by W. M. Nagle, in partial fulfillment of the requirements for the degree of Doctor of Science.

the type of condensation to which they apply. The problem thus divides itself into two parts both of which are replete with difficulties of technique and observation: the measurement of heat transfer coefficients, and the study of wettability under non-isothermal conditions. It is impossible at this time to present a complete report of all phases of the work, but the practical importance of some of the results merits a progress report.

Review of the Literature

Schmidt, Schurig, and Sellschopp, the pioneers in the study of the differences between film and drop-wise condensation, condensed steam on one face of a vertical copper disc 1 mm. (0.039 in.) thick by 15 cm. (5.91 in.) in diameter, while the other side was cooled by a high-velocity jet of water directed against the center of the disc by a calibrated nozzle 3.9 mm. (0.15 in.) in diameter. The effective heat transfer area was that of a circle 13.4 cm. (5.28 in.) in diameter. The steam chamber was built in part of glass to permit inspection of the process of condensation. The method of cooling adopted resulted in a low thermal resistance on the water side so that variations in the steam-side coefficient of heat transfer could be recognized with certainty. Steam was supplied saturated at approximately 1.1 atm. The inlet temperature of the cooling water varied only from 10° C. (50° F.) to 13° C. (55° F.). The amount of heat transferred was determined solely from the rate and temperature rise of the cooling water. The plate temperature could be found by explorations on the water side with a movable copper-constantan thermocouple.

When the steam-side of the copper plate had been etched with zinc chloride dissolved in hydrochloric acid, the steam condensed in a complete film, and the overall coefficients of heat transfer ranged from 890 to 985 B.t.u./(hr.) (sq.ft.) (° F.) as the velocity of the water leaving the nozzle increased from 16.4 to 36 ft./sec. However, after long use, spots of drop-wise condensation appeared, "produced possibly by dirt or little drops of oil brought in with the steam." One series of runs on an etched copper disc shows that the film area increased from 30% to 100% as time went on; later there was a decrease to 98%.

In two series of runs in which steam condensed on freshly polished copper, the condensation was completely drop-wise, and the overall coefficients increased rapidly from 1600 to 3140 B.t.u./(hr.) (sq.ft.)

(° F.) as the velocity of the water jet increased from 9.5 to 35.7 ft./sec. At the highest water velocity, the rate of condensation was enormous, 430 pounds of steam per hour per square foot. The individual steam-to-metal coefficients, h_s, reported for drop-wise condensation are listed in Table I together with the data for one run with film condensation. The value of h_s obtained with film condensation, 1360 B.t.u./(hr.) (sq.ft.) (° F.), agrees fairly well with the value of 1200 calculated from the theoretical formula of Nusselt.[15] The values of h_s for drop-wise condensation are 5 to 7 times the values predicted from Nusselt's formula. The actual condensation rate for drop-wise condensation is 1.9 to 2.5 times that obtained with film condensation.

TABLE I

Steam-Side Coefficients for Vertical Copper Disc
(Schmidt, Schurig and Sellschopp).

Type of Condensation	Nozzle Veloc.		Water Inlet		Steam Temp.		Condensation Rate		Steam-side Coefficient, h_s	
	m./sec.	ft./sec.	° C.	° F.	° C.	° F.	Kg./(hr.)(sq.m.)	lb./(hr.)(sq. ft.)	K. Cal./(hr.)(sq.m.)(° C.)	B.t.u./(hr.)(sq. ft.)(° F.)
Drop-wise	5.0	16.4	11.1	52.0	100.6	213.1	1410	289	39050	8000
Drop-wise	7.7	25.2	10.5	50.9	101.0	213.8	1860	381	42200	8650
Drop-wise	9.2	30.2	10.2	50.4	100.3	212.5	1830	375	30900	6350
Film	6.0	19.7	10.6	51.1	101.0	213.8	736	151	6650	1360

Schmidt, Schurig, and Sellschopp also obtained drop-wise condensation on freshly polished copper made oily with a light film of kerosene. In a preliminary run before installing a steam strainer, a shiny (*blanke*) copper disc gave drop-wise condensation at first, although film condensation appeared later at places where iron rust from the steam accumulated. A light layer of kerosene on a shiny (*blanke*) copper disc gave drop-wise condensation for a time, but the effect did not last, presumably because the kerosene was washed off. Lubricating oil and grease were said to be unsuited. The most lasting drop-wise condensation was given by chrome-plated polished copper. In connection with the last observation, it is interesting to recall that Jakob and Erk [13] in 1928 noted that impermanent drop-wise condensation of steam occurred on a tin-plated surface.

In their summary, Schmidt, Schurig, and Sellschopp held that steam condensed in the form of a continuous film on "dirty surfaces and surfaces roughened by etching," and condensed in the form of

drops on "clean and smooth surfaces." Unfortunately, no hint is given in their article of the way in which the surfaces were cleaned or polished.

The most comprehensive investigation of drop-wise condensation yet reported was published in 1931 by H. J. Spoelstra.[17] He observed and sought to explain a curious heat transfer phenomenon found when testing fouled tubes from evaporators in Javanese sugar mills: Copper or brass tubes from the first effects often showed an increase of thermal resistance on cleaning. Table II exemplifies the results. The coefficients U_f were determined for a tube removed from the first effect of an evaporator just before cleaning. The steam chest of the evaporator was then cleaned with naphtha according to the practice in Java; and a second tube, removed immediately afterward, gave the coefficients U_c. Analysis showed that the original scale contained from 15% to 30% of oily substances which were largely removed by the naphtha. The resultant scale was somewhat porous.

TABLE II

Effect of Cleaning with Naphtha (Spoelstra)
(Average of 12 tests for each pressure)

Steam Temp		Gage Pressure		Overall Coefficient B.t.u./(hr.) (sq.ft.)(°F.)		$\frac{U_f - U_c}{U_f}$ %
° C.	° F.	Kg./ sq.cm.	Lbs./ sq. in.	Fouled U_f	Cleaned U_c	
110.8	231.4	0.5	7.1	411	298	27
112.7	234.9	0.6	8.5	508	346	32

That different tubes might be compared under essentially identical conditions, for the above tests and for those of Tables III and IV below, Spoelstra used duplicate experimental evaporators. In each unit 100 cm. (39.4 in.) of the tube to be tested served as a vertical steam-jacketed riser through which water from a suitable reservoir was re-circulated, filling the tube.

Table III shows the results of a comparison between cleaned and fouled brass and copper tubes from various effects in sugar mills E and F. The cleaned tubes, numbered 1a, 3a, 6a, 10a and 11a were carefully scoured, slightly polished, and freed of oil by washing in naphtha; after washing the surface was not touched. Also, all tubes were well scoured inside.

TABLE III

Comparison of Scale-free Tubes with Fouled Tubes (Spoelstra)

Mill	Effect	Tube No.		Material	Diameters Inches		Nature of Fouling	Quantity of Scale mg./sq.cm.	% Oil in Scale	Surface of Clean Tube	Steam Pressure (Gage)		Overall Coefficient B.t.u./(hr.)(sq.ft.)(° F.)		$U_f - U_c$ / U_c — %
		Clean	Fouled		I.D.	O.D.					Kg./sq.cm.	lb./sq.in.	Clean, U_c	Fouled, U_f	
E	I	1a	1	Brass	1.22	1.38	Thin black, very smooth	0.44	34.26	.....	0.5	7.1	640	673	+ 5
		1a	2								0.5	7.1	609	959	+57
F	I	3a	3	Copper	1.26	1.38	Thin, black, very smooth	0.40	18.28	.....	0.5	7.1	664	767	+15
		3a	4								0.5	7.1	645	826	+28
E	III	6a	6	Brass	1.30	1.42	Slight; gray, thin, smooth layer	0.53	2.58	Dezinced; red copper color, somewhat gray and dull	0.5	7.1	486	356	−27
											0.6	8.5	560	418	−25
											0.7	9.95	704	468	−34
F	III	10a	10	Copper	1.26	1.38	Slight; black, rather smooth surface	0.42	6.68	In part lightly corroded	0.5	7.1	524	351	−33
											0.6	8.5	705	462	−34
											0.7	9.95	820	504	−39
F	IV	11a	11	Copper	1.26	1.38	Very slight; black, even surface	0.28	6.41	In part lightly corroded	0.5	7.1	506	397	−21
											0.6	8.5	639	433	−32
											0.7	9.95	748	489	−35

The tests summarized in Table II show that the presence of oil in the scale markedly increases the coefficient of heat transfer above that obtainable with the same scale, when oil-free. The tests of Table III show further that a tube with a thin scale, if very oily, has a higher coefficient of heat transfer than even a scale-free tube. However, it is clear from the tests on tubes 6, 10 and 11 that fouling with a slightly oily scale produces the normal result: a decreased coefficient. The further experiments on Tubes Nos. 3a and 4, shown in Table IV, confirm the conclusions drawn from Table III. Polishing was found to increase the coefficients, but unfortunately Spoelstra did not report the details of the method of polishing.

TABLE IV

Influence of Cleaning Methods on Overall Coefficient (Spoelstra)

Run No.	Treatment		Overall Coefficient B.t.u./(hr.)(sq.ft.)(°F.)		$\frac{U_4-U_{3a}}{U_{3a}}$ %
	Tube No. 3a	Tube No. 4	No. 3a U_{3a}	No. 4 U_4	
A	Scoured, polished and naphtha cleaned (See Table III)	Original fouled tube (See Table III)	645	826	+28
B	Scoured smooth again	Washed with naphtha	597 604	500 517	−16 −14
C	Scoured smooth again	Scoured clean and polished	601 589	736 718	+23 +22
D	Polished anew	Polished anew	670 632 641	689 618 644	+ 3 − 2 + 0.5

Steam Pressure was 0.5 Kg./sq. cm. (7.1 lbs. sq. in.) gage.

In order to study further the favorable effect of oil, Spoelstra ran heat transfer tests of about three weeks duration on four originally oil-free tubes, using oil-free steam for the first part of each run and steam into which oil was injected for the rest of the run. With two of these tubes, one a clean uncorroded brass tube (Tube No. 1a of Table III), the other a slightly fouled tube from the first effect (Tube No. 1 of Table III) but made oil-free, the injection of oil into the steam caused a marked increase in the overall coefficients. The coefficients did not remain at their highest value, but decreased gradually, although the injection of oil was continued. Nevertheless, the thermal resistance remained less than that obtaining at the start. When two other tubes, one an entirely clean but severely pitted tube originally from the second effect of mill E, and the other a badly fouled

tube from the second effect of mill F, were tested, the favorable effect of oil injection was not marked.

The tests described above were completed before the article by Schmidt, Schurig, and Sellschopp appeared in 1930. Spoelstra originally supposed the increase in heat transfer on oily surfaces to be caused by a "faster flow of condensate" over the oily surface or to a possible breaking of the condensate film and formation of irregular channels leaving parts of the tube dry. After the appearance of the article by Schmidt, Schurig and Sellschopp, Spoelstra built a small apparatus (Fig. 1) in which the manner of condensation could be

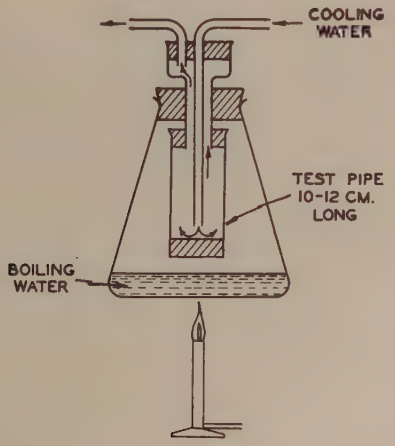

FIG. 1. Glass apparatus of Spoelstra.

observed. Short test-lengths cut from the copper and brass tubes examined previously, were tested in this apparatus to determine whether the type of condensation was film or drop-wise. No coefficients of heat transfer were reported. The results of these tests were summarized by Spoelstra, as follows:

"1. On a clean copper or brass tube, film, drop-wise, or mixed condensation can take place. Copper and brass tubes behave equally in this regard.

"With clean tubes the form of condensation cannot always be predicted with certainty. Nevertheless, it holds that, in general, film condensation is to be expected on somewhat rough or scratched surfaces and also on dezinced tubes and tubes at-

tacked in other ways; and drop-wise condensation on smooth, well polished surfaces. The roughness of a tube surface need not always be visible to the naked eye.

"2. If we have a clean tube giving drop-wise condensation, film condensation can be obtained by scouring the tube with fine emery cloth. The tube then has very fine scratches.

"On the addition of a little oil, this film condensation returns to drop-wise condensation. Although the experimental apparatus was not well suited for making exact measurements, yet we could always notice from the outlet cooling water temperature that, for the same tube, the heat transfer coefficient is higher with drop-wise condensation.

"3. Tubes with a porous (oil-free) scale always exhibit film condensation, although this scale may seem very thin, and to the eye, very even. By means of oil this film condensation can in many cases be changed entirely or partially to drop-wise condensation.

"4. Tubes with such a strong fouling that the surface is uneven and rough always exhibit film condensation. In general it is not possible to obtain drop-wise condensation in this case by oiling.

"5. Various degrees of intensity of drop-wise condensation may be recognized. In general we found the finest drop-wise on the very smooth and at the same time oily surfaces.

"6. With pure drop-wise condensation, the flow of condensate is considerably better than with film condensation. The latter seems always controlled by the roughness of the surface and the larger or smaller tendency for water to stick."

In order to determine visually whether drop-wise condensation also occurred on long vertical tubes, Spoelstra installed a peep glass in the lower part of one of the two steam chambers of his laboratory evaporator. In this apparatus tests were run on tubes one meter long. One tube was scoured clean, polished, and inserted in the steam chamber. At the start of the run, the lower part of the tube showed drop-wise condensation, which, however, soon changed to film condensation. A little oil was then injected with the steam, and within a short time spots of drop-wise condensation appeared, grew, and covered the entire visible part of the tube. In this run during drop-wise condensation the overall coefficient from condensing steam to boiling water was $U_D = 633$ B.t.u./(hr.)(sq.ft.)(° F.). The steam pressure was 7.1 lb./sq. in. gage. The tube was next removed, rubbed down with fine emery cloth, and made oil-free. Then, on testing, only film condensation was seen through the peep glass, and the coefficient was

found to be $U_F = 524$. Oil was again introduced into the steam, and on the visible part of the tube the condensation was again drop-wise with the coefficient $U_D = 618$. When the steam pressure was raised from 7.1 lb./sq. in. gage to 9.95 lb.sq. in. gage, the condensation remained drop-wise and the coefficient increased to 941.

In the same year in which Spoelstra published these data demonstrating the favorable effect of oil in condensing steam, R. P. Tobin [18] concluded that oil in steam reduces the heat transfer. He had no data, but based his conclusion on the assumption that the oil film could be considered as an added series resistance to the heat current.

In 1932, Jakob [11] gave a brief report of an investigation of drop-wise condensation of steam by F. Roecke at the Bitterfeld Works of the I.-G. Farbenindustrie. Roecke's apparatus was an experimental evaporator, consisting of a steam-jacketed vertical tube 1250 mm. (4.1 ft.) long and 53 mm. (2.09 in.) in outside diameter. The steam jacket was provided with sight glasses, through which the outer surface of the tube could be lighted, observed, and photographed. The material of the tube was not given. The type of condensation was seen to be drop-wise or mixed, even when the tube surface was made mat with the finest emery cloth. Only after the tube had been washed for 56 hours with carbon tetrachloride was it possible to hold a water film for 40 hours. Pipe temperatures were measured and individual coefficients were determined for drop-wise and for film condensation of steam. These coefficients were said to agree with the results of Schmidt, Schurig, and Sellschopp. Roecke also observed drop-wise condensation with superheated steam, although the drops were flatter, grew more slowly, and stuck to the surface longer before starting to run down. The rate of heat transfer was less than for drop-wise condensation with saturated steam.

Jakob [12] wrote that drop-wise condensation of steam perhaps always occurs on oily, non-wettable surfaces; film condensation on rough surfaces; and that both types of condensation might occur on clean smooth surfaces. He surmised that the direction and velocity of the steam might be important in determining the type of condensation. Jakob made some qualitative measurements which led him to believe that film condensation occurs when steam is flowing parallel to the cooling surface at high velocities, but that mixed condensation is the rule at low steam velocities. The behavior of condensing steam was said to depend also on the cleanliness and characteristics of the surface.

In a current paper C. G. Kirkbride [14] states that drop-wise condensation "is undoubtedly a function of the surface tension and the mass rate of condensation per unit area. This can be observed by condensing a light hydrocarbon such as gasoline on a glass tube and comparing it with the condensation of steam and also aniline. Gasoline will form a condensate film at the lower condensation rates because of its low surface tension but steam and aniline will form in drops due to their high surface tension. Nevertheless, upon increasing the condensation

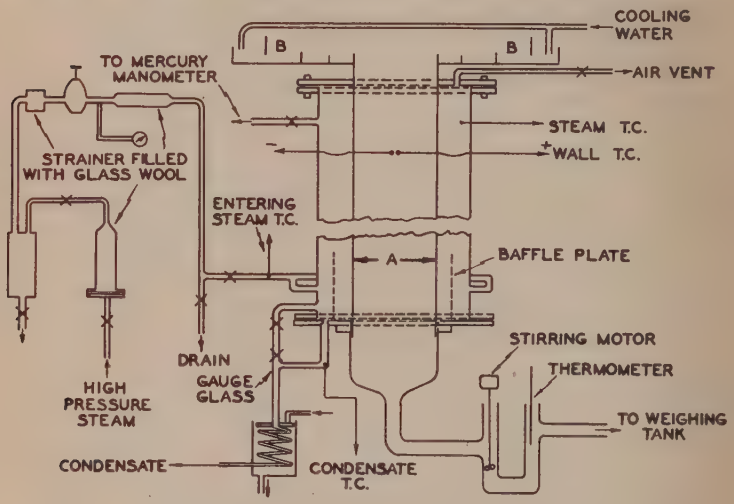

FIG. 2. Diagrammatic sketch of large condenser.

rates of steam and aniline they can be made to condense as a film on the tube."

The available data establish clearly that the individual coefficient for drop-wise condensation of steam is many times larger than that for film condensation, both on short vertical tubes and plates and on vertical tubes over one meter long. Although there is considerable uncertainty and disagreement as to the behavior of condensing steam in a given circumstance, and as to the best method of obtaining drop-wise condensation, this general statement may be made: Rough and oil-free surfaces tend toward film condensation, while smooth and oily surfaces tend toward drop-wise condensation. As a result, the formation of an oily scale may increase the rate of heat transfer rather than decrease it.

There are practically no data on the type of condensation obtained when condensing vapors other than steam.

New Data

Change of Heat Transfer with Time

Large Condenser.—As previously remarked the present work was started in an attempt to explain an increase with time of the capacity of the falling-film condenser sketched in Fig. 2. Boiler steam was condensed on the outside surface of the standard 2½-inch iron-pipe-size copper pipe A exposed for 24 inches of its length. Cooling water entered the head box B from a constant-head tank, overflowed the lip of a short bakelite section above the copper pipe, and flowed down the inside of the copper pipe in a smooth film. The water leaving the condenser passed through a motor-driven stirring device followed by a thermometer and into a weighing drum. The inlet water temperature was measured in the head box. The steam pressure and inlet temperature, the condensate temperature, and the rate of condensation were measured. The pipe temperature was measured in ten places by means of thermocouples soldered in grooves on the steam-side surface of the pipe.

Figure 3 shows the startling increase of heat transfer with time during four consecutive runs in each of which the imposed conditions were held substantially constant. During the first period of shutdown between runs the steam chamber was full of condensate; during the second, full of steam; and during the third, full of air. The overall coefficients U are based on the arithmetic mean of the inside and outside heat transfer areas and are calculated from the heat picked up by the cooling water. The heat lost by the steam agreed with that gained by the water within an average deviation of 2%, the maximum deviation being 5%.

Simultaneously with the increase in the rate of heat transfer, the temperature of the pipe wall also increased. The thermocouple readings varied with location and with time, but that there was an increase of wall temperature is unmistakable. Figure 4 shows how the pipe temperatures and heat throughout changed with time during Run 2. The thermocouples are numbered in pairs from 1 to 5 starting at the top of the test pipe; a and b refer to members of a pair situated diametrically opposite each other at the same level. By averaging the

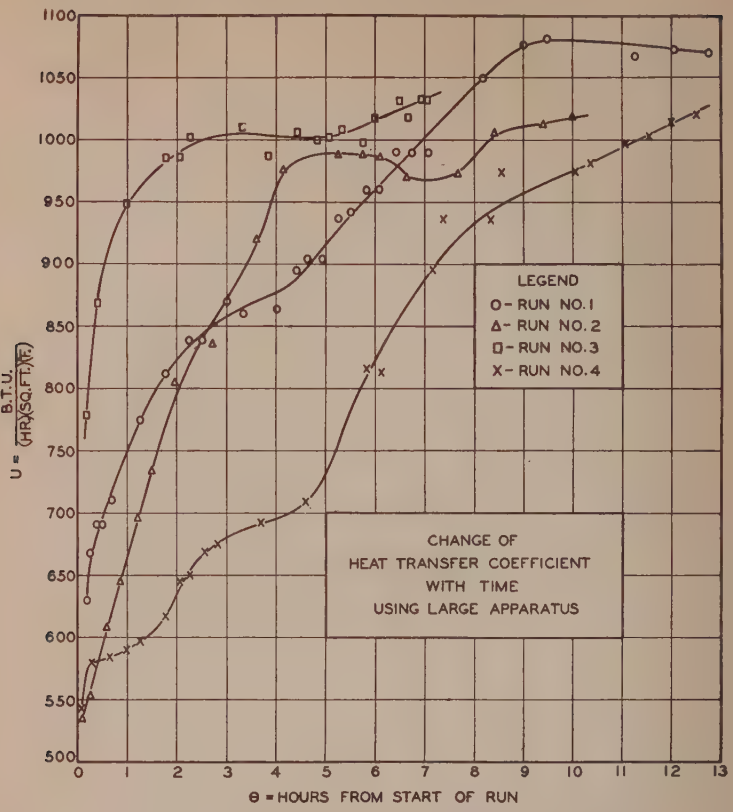

FIG. 3. Overall coefficients of heat transfer obtained in large condenser with steam condensing on a copper pipe.

Run No.	*History*	*Steam Pressure lbs./sq. in. gage*	*Range of water rate lb./hr.*	*Range of water inlet temp. ° F.*
1.	Outside surface freshly cleaned using fine emery cloth and solution of $ZnCl_2$ and HCl.	5.1	2035 to 2070	42 to 43
2.	Steam chamber was left overnight full of condensate.	5.2	2035 to 2085	43 to 45
3.	Steam was allowed to flow through steam chamber over weekend. Water was turned off.	5.1	2060 to 2090	44.5 to 47.5
4.	Steam chamber was open to the air for 14 days.	5.2	2040 to 2090	48 to 50

pipe temperature readings to obtain a mean temperature, some idea of the change of steam side coefficient can be obtained. For the run presented in Fig. 4, the steam side coefficient was roughly 1400 B.t.u. /(hr.)(sq.ft.)(° F.) one-half hour after the start of the run and 3700 B.t.u./(hr.)(sq.ft.)(° F.) nine hours after the start.

Three days after the fourth run was made the copper pipe was removed, and water was poured over it. Some areas wet readily,

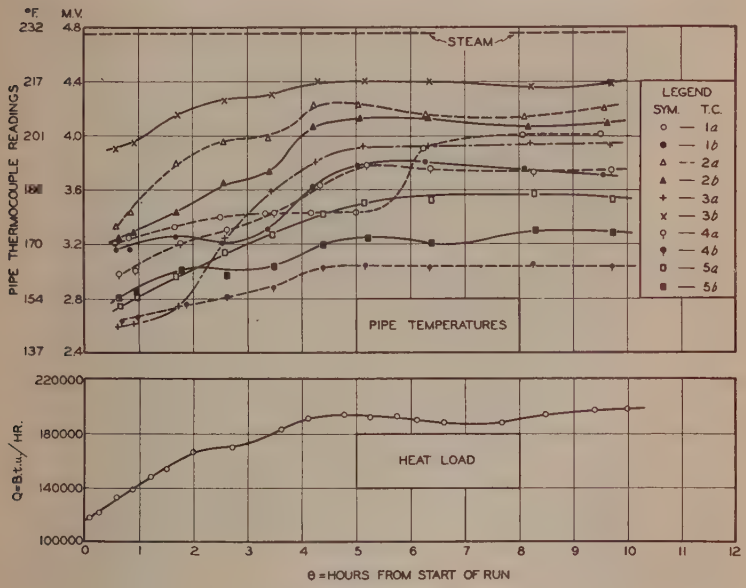

FIG. 4. Change of heat load and pipe temperatures with time during Run No. 2 on large condenser.

others did not. In general, the areas giving the lowest thermocouple readings at the end of the fourth run were the most readily wet. Although no visual observations of the copper tube were possible during a run it is probable that film condensation had occurred on the wettable areas and drop-wise condensation on the non-wettable areas. Such a circumstance would explain the apparently anomolous variations among the simultaneous readings of the several thermocouples. The observed increase in heat transfer could be explained if there had been an increase in the ratio of drop-wise area to film area. In order to

determine if such were really the case a glass jacketed apparatus was needed.

Small Condensers.—As a consequence of the puzzling results found with the large condenser, Billings and Wadt [4] in co-operation with the authors devised the twin falling-film condenser units shown in Fig. 5. The members of the pair are identical with each other.

The steam jacket for each unit consisted of two concentric pyrex glass cylinders, 6 inches long by 5½ and 6½ inches in diameter. They were closed by steel plates held together by tie rods, the joints between the plates and the inner cylinder being made tight by means of rubber

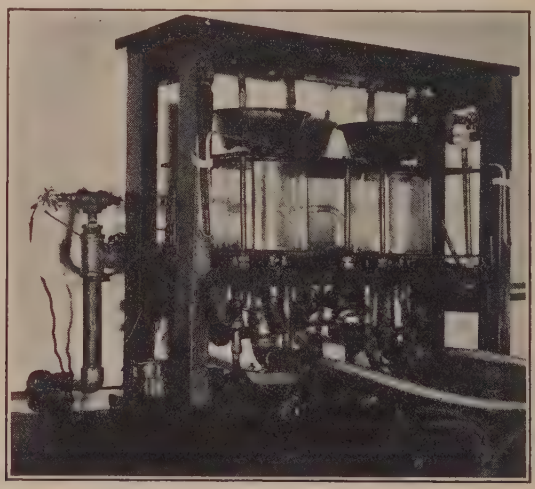

FIG. 5. Glass-jacketed condenser.

gaskets. The heat transfer tubes, 1 inch O.D. by 10 inches long, were inserted through 1½ inch holes in the center of each steel plate. The tubes were held in place by rubber stoppers. The steam, taken from a tee just preceding the manifold in the large apparatus, Fig. 2, had passed through two glass-wool strainers. After passing through water separators the steam entered the inner jacket of each unit through two iron nipples that projected through the bottom steel plate. A separate valve controlled the steam to each unit. An air vent, a manometer, and a condensate outlet were provided. To prevent fogging of the glass jackets superheated steam was passed through the annular space between them.

The cooling water for each unit was fed into a head box made from an angel-cake tin whence the water flowed over the lip of the heat transfer tube, down the inside of the tube as a film, and passed to a weighing tank. The joint between the head box and the heat transfer tube was made tight with chewing gum, which proved to be entirely satisfactory and permitted easy removal of the tube.

In Table V is given a list of the tubes tested in the small condensers together with their dimensions and the value of the thermal conductivity, k, that was used in estimating the temperature drop through the tube wall. All tubes were 1 inch O.D. by 10 inches long and the length of the heating section was 6¼ inches. The steam pressure was usually held between ½ and 1 inch of mercury gage.

TABLE V

Material	No. of tubes tested	Thickness inches[1]	k B.t.u./(hr.) (sq. ft.) (°F.)	L/k (°F.) (sq. ft.) (hr.)/B.t.u.
Copper	1	0.080	222*	0.000030
Brass (20 gage)	1	0.028	63*	0.000037
Brass (28 gage)	1	0.018	63*	0.000024
Nickel	1	0.034	33.8**	0.000084
Monel Metal	1	0.036	10.4**	0.00029
Steel	2	0.065	33*	.....
Aluminum	1	0.037	119*	0.000026
Chrome plated copper	1	0.080	222*	0.000030
Chrome plated brass	1	0.017	63*	0.000022
18–8 Chrome nickel steel	1	0.059	10***	0.00049

1. Thickness reported is average of several readings with a tubing micrometer.
* Heat Transmission, W. H. McAdams, 1st Ed., p. 308.
** Int. Nickel Co., Private Communications (1933).
*** Babcock & Wilcox Catalog (1929).

Tests in the small condensers on tubes of copper and brass confirmed the assumptions made above that the increase of heat transfer observed during runs on the large apparatus was due to a change from film to drop-wise condensation. Sometimes it took days for an appreciable change, sometimes only a few minutes. In Figures 6 and 7 are presented data on smooth tubes of copper and brass which had been cleaned with precipitated chalk. In order that the heat transfer data obtained on tubes of different metals and of different wall thicknesses might be comparable, the overall coefficient of heat transfer, U, was corrected for the thermal resistance of the wall. The corrected overall coefficient, U', was calculated by the equation

$$\frac{1}{U'} = \frac{1}{U} - \frac{L}{k}$$

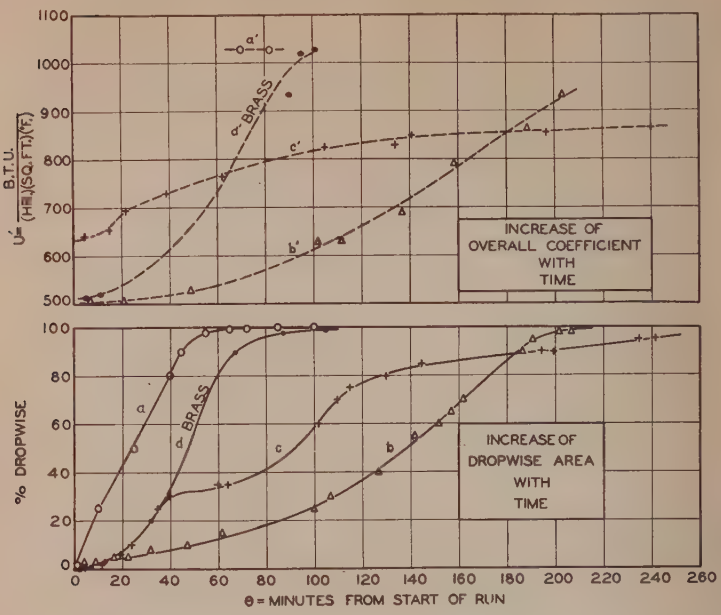

FIG. 6. Change from film to drop-wise condensation and the corresponding increase in the overall coefficient of heat transfer: cleaned, smooth copper and brass.

Curves *a* and *a'*. Copper tube buffed smooth on cloth wheel with commercial emery and fat buffing compound, then cleaned with precipitated chalk on wet cloth. Surface was wettable with cold water before the run, non-wettable after.

Curves *b* and *b'*. Smooth copper tube cleaned again with precipitated chalk. Wet with cold water.

Curves *c* and *c'*: Above tube after 15 hours shut-down. After the run 95% of the surface was non-wettable, corresponding to the 95% that gave drop-wise condensation at end of run.

Curves *d* and *d'*. Brass tube made fairly smooth by scouring with FFF emery flour and by cleaning with precipitated chalk. Wet with cold water.

Curve	*Rate, lb./hr.*	*Water Inlet, ° F.*	*Heat Load, B.t.u./(hr.) (sq.ft.)*
a'	570	69	131000
b'	575—615	69—69.5	68500—120000
c'	540—635	69—70	84000—112000
d'	555—685	76.5	66000—115000

where L is the tube thickness and k, the thermal conductivity. The coefficients given are based on the arithmetic mean area, the arithmetic mean temperature difference, and the heat picked up by the water. From Fig. 6 it may be seen that corresponding U' vs. θ and *% drop-wise* vs. θ curves have similar shapes and increase together.

The water rate for a series of heat transfer measurements was not

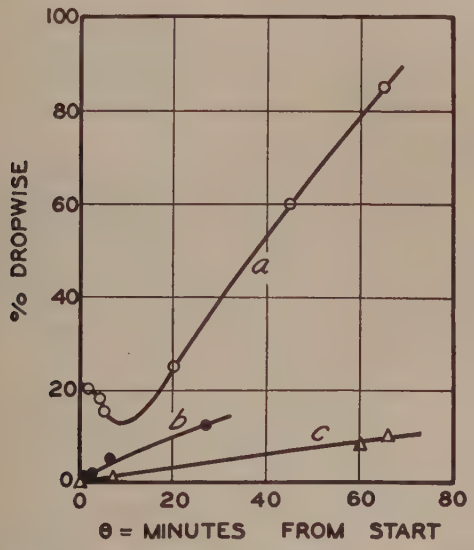

FIG. 7. Change of per cent drop-wise area with time: smooth, cleaned copper and brass.

Curve *a*. Copper tube, highly polished with wet rouge on felt and with dry rouge and oleic acid on cloth, and cleaned with precipitated chalk on wet cloth. Surface wet with cold water.

Curbe *b*. Above tube after a shut-down of 5 hours.

Curve *c*: 20-gage brass tube, polished with red oxide of iron on wet cloth and cleaned with precipitated chalk. Surface wet with cold water. However, after the run the surface was non-wettable on areas that gave drop-wise condensation at the end of the run.

always constant. However, runs made in the small condenser on tubes giving 100% drop-wise or 100% film condensation gave less than 15% variation in U when the water rate was varied between 250 and 730 lbs./hr. This is in agreement with a large number of preliminary runs made with the large condenser, and with the results of Gaylord and Kennedy [8] who used a similar apparatus. The data

plotted in Fig. 8 show how small is the effect of water velocity on U'. In order to illustrate the heat balances obtainable with the small condenser, the plot includes the values of U' calculated from the heat given up by the steam. The effect of time was minimized by rapid

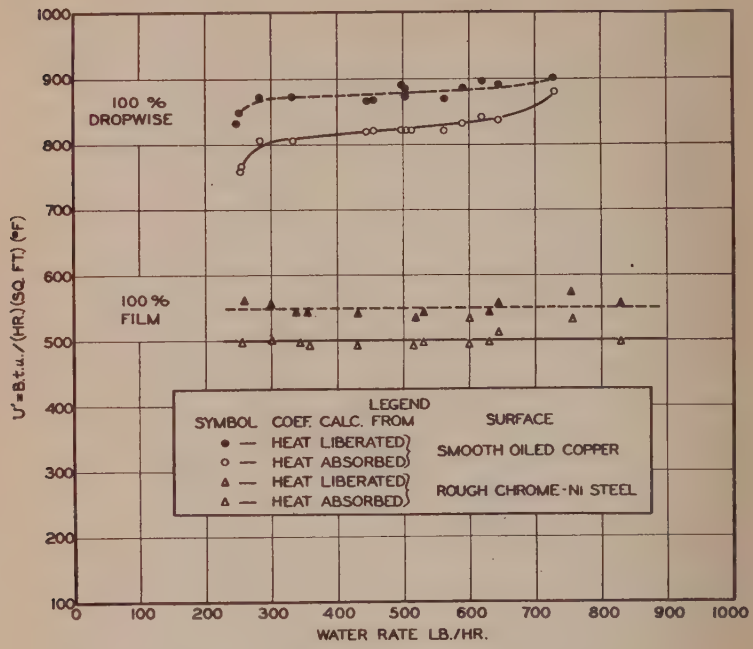

FIG. 8. Effect of water rate on the overall coefficient of heat transfer.

Copper tube, buffed with Tripoli polishing compound, cleaned thoroughly in hot caustic solution, and given a film of "fuel oil."

Chrome-nickel steel tube, with original, very rough surface, was washed and given film of "fuel oil."

Tube	*Inlet-Temp., °F.*	*Heat Load B.t.u./ (hr.) (sq.ft.)*
Copper	59—60	95000—120000
Chrome-nickel	59—60	57000— 68500

work. For each kind of condensation the range of water velocities was covered twice, once with increasing velocities and once with decreasing velocities. The data on 100% drop-wise condensation were obtained with the copper tube of which the surface had been buffed and wiped with an oily rag. The data on film condensation were ob-

tained on a rough chrome-nickel steel tube, which, though it had been wiped with an oily rag, nevertheless gave film condensation due to its extreme roughness.

The rate of change from film to drop-wise condensation is most erratic, varying no doubt with the preparation of the surface and possibly with impurities in the steam. The data of Curve *a*, Fig. 7, obtained on an extremely smooth copper surface, show a rapid increase of per cent drop-wise condensation with time, after a decrease in the first five minutes of the run. Yet another run on the same tube, the surface of which had been buffed, and subsequently cleaned in a boiling caustic solution, gave film condensation throughout a five-hour run, see curve c, Fig. 9. The caustic solution was made up as follows:

1 gallon of water
4 ounces of soda ash
2 ounces of tri-sodium phosphate
½ ounce of soap
½ ounce of caustic soda

Two additional runs are plotted in Fig. 9, both of more than sixty hours' duration. Curve *a* for rough brass giving film condensation throughout shows a gradual decrease in the coefficient of heat transfer, probably due to scale formation. Curve *b*, Fig. 9, for smooth copper shows that U increases when the percentage of drop-wise condensation increases rapidly, but decreases slowly with time when the type of condensation undergoes no considerable change. Again, the slow decrease may be attributed to scale formation.

Run *c* of Fig. 6 was a continuation of Run *b* after a shutdown of 15 hours during which the steam space was filled with air. Similarly in Fig. 7, Run *b* was a continuation of Run *a* after a shutdown of 5 hours. In both cases film condensation was obtained immediately after shutdown, although drop-wise condensation existed prior to shutdown. Moreover, Fig. 6 shows a corresponding decrease in the coefficient of heat transfer from 930 to 630 B.t.u./(hr.)(sq.ft.)(° F.). It will be recalled from Fig. 3 that the large condenser showed a similar drop in the rate of heat transfer following shutdown. Furthermore, in the case of the large condenser, the drop occurred whether the steam chamber had been left full of air, full of steam, or full of condensate during shutdown. These experiments

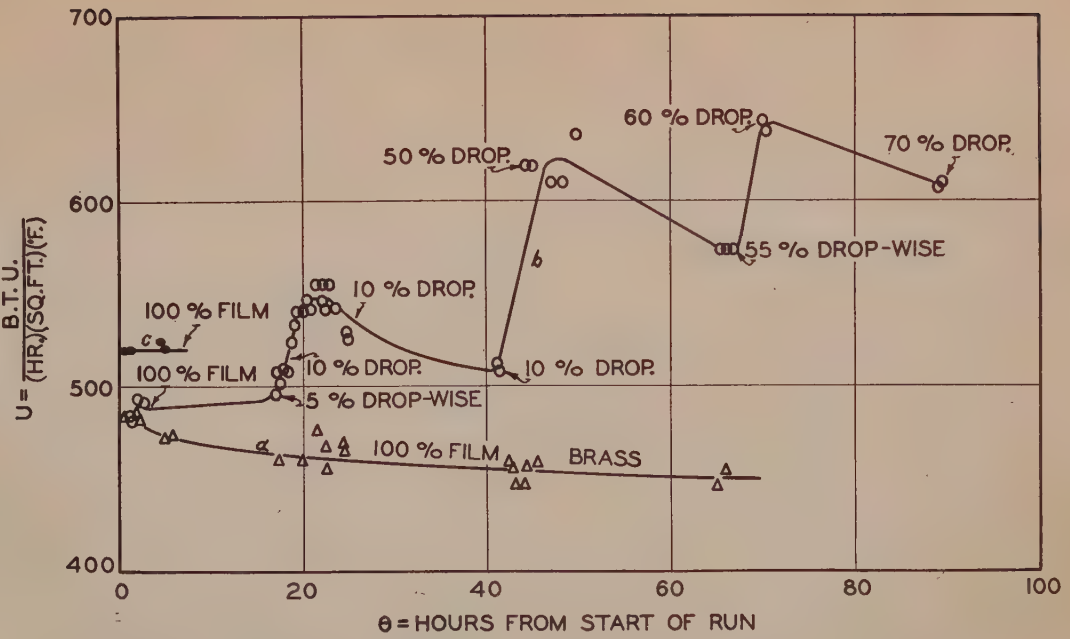

FIG. 9. Effect of length of run: smooth copper and rough brass.

Curve *a*. 28-gage brass tube, roughened with emery cloth and washed in "Gresolvent." Wettable in cold water.

Curve *b*. Copper tube, polished on buffing wheel with commercial Tripoli and fat compound. Washed in hot caustic solution. Wettable to cold water.

Curve *c*. Copper tube, polished on buffing wheel with Tripoli and washed in hot caustic. Wettable to cold water.

Curve	*Water Rate* *lb./hr.*	*Inlet Temp.* *°F.*	*Heat Load* *B.t.u./(hr.)(sq.ft.)*
a	570—600	56—58	71500—92500
b	555—580	55—57	68000—75000
c	560—635	58—59	75500—76500

show conclusively that the increase in heat transfer with time observed with the large condenser may be ascribed to a change from film to drop-wise condensation. Analogously the drop in the rate of heat transfer occasioned by shutdown was caused by a change from drop-wise to film condensation. Possibly the increase of drop-wise area during operation is caused by oil brought in by the steam. For the change during shutdown the authors know of no satisfactory explanation. Experiments are now in progress in an attempt to clear up these points.

Effect of Surface Treatment on Condensation

Copper and Brass.—In the case of polished copper and brass, cleaned by soaking in hot caustic solution or by rubbing with precipitated chalk on a wet cloth, film condensation was generally observed at the beginning of a run (Figs. 6, 7 and 9). The most lasting film condensation followed the treatment with caustic (curves b and c, Fig. 9). However, as has been seen, this type of condensation was not permanent on smooth surfaces.

Drop-wise condensation is promoted by treating the surface with oil or fat.

The following oils and fatty materials were used:

Russian Mineral Oil (McKesson and Robbins)
Specific gravity between 0.83 and 0.89 at 25° C.
Viscosity 571 to 587 Saybolt at 25° C.
"Fuel Oil," an undetermined mixture of oils used at M.I.T. for Diesel fuel
Kerosene
Mutton tallow
Beeswax
Olive oil
Stearic acid
Oleic acid
Fatty binders of two commercial buffing compounds (emery and Tripoli)

Before applying an oil or fat, the surface of the tube was cleaned, usually by washing in hot caustic solution or by rubbing with precipitated chalk on a wet cloth until the surface held a film when immersed

in water and allowed to drain. Oil and fatty compounds were then applied to the outside surface of the tube by rubbing with a cloth and some of the compound. The application of solid compounds was facilitated by heating the tube.

No oil or fat gave 100% drop-wise condensation every time it was used. Mixed condensation was frequently observed. In all cases of mixed condensation on copper and brass, the per cent drop-wise condensation increased as the run progressed in the manner described in the preceding section for cleaned copper and brass. The increase was usually more rapid on oily surfaces. A decrease in per cent drop-wise area during the first few minutes of a run, as illustrated for cleaned copper by Curve a, Fig. 7, was also observed in several runs on copper or brass treated with oils and fats. Likewise the per cent drop-wise condensation or oily surfaces frequently became less during periods of shut-down. In some cases a change from 100% drop-wise to complete film occurred during shut-down.

On smooth surfaces a thin film of oil or fatty compound had a large effect in promoting drop-wise condensation from the start of the run. It was found that drop-wise condensation was obtained from the start after the copper tube had been buffed smooth on a cloth wheel with Tripoli and a fatty binder as a polishing agent, and wiped with a cloth dipped in "fuel oil." (See photograph, Fig. 10a, and curve A, Fig. 11). Sometimes the fatty binder was removed from the surface of the copper with hot caustic solution before the "fuel oil" was applied. (See Fig. 8). In many runs, however, the use of fuel oil on smooth surfaces gave mixed condensation, not 100% drop-wise, near the start. Russian mineral oil did not give as satisfactory drop-wise condensation as did the "fuel oil." Mutton tallow was tried on one run, and, although the surface was decidedly non-wettable to cold water before the run, film condensation resulted. It appeared in many cases that the failure to obtain at least 50% drop-wise condensation was caused by too thick a layer of oil or fat. A thin adsorbed film was found more satisfactory. The fatty binder in the Tripoli buffing compound, whether applied on the buffing wheel or on a cloth, was decidedly better than Russian mineral oil or "fuel oil." Beeswax was much better than the petroleum oils, as also was oleic acid. One hundred per cent drop-wise condensation was obtained from the start to the end of a run on the copper tube which had been polished to a high lustre with rouge and oleic acid on a clean cloth.

The excess of these polishing agents had been removed by wiping with a fresh cloth. The 20-gage brass tube as received was fairly smooth, and was found to give 100% drop-wise condensation after

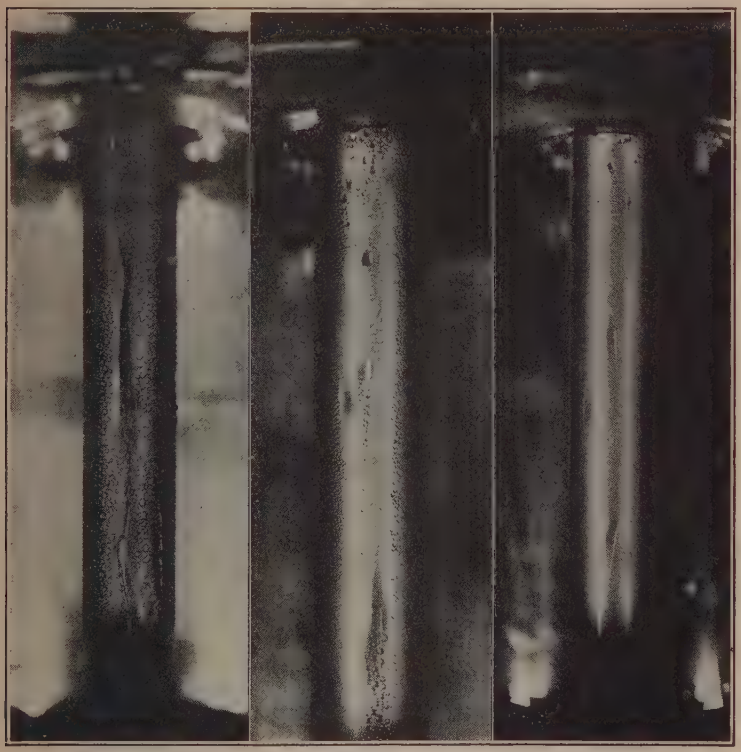

FIG. 10. Photographs of drop-wise condensation, illuminated by means of photo-flash bulbs.

a. Copper tube, buffed and oiled with "fuel oil." A continuous stream of condensate may be seen near the center of the photograph.

b. Chromium-plated copper, washed with soap and water.

c. Chrome-nickel steel, ground smooth, polished with red oxide of iron in water and with precipitated chalk in water, and given a thin film of oleic acid. The drops are very small.

treatment with oleic acid, with no preliminary surface treatment other than cleaning with precipitated chalk (Curve B, Fig. 11). A run on polished brass treated with oleic acid is shown as Curve C, Fig 11.

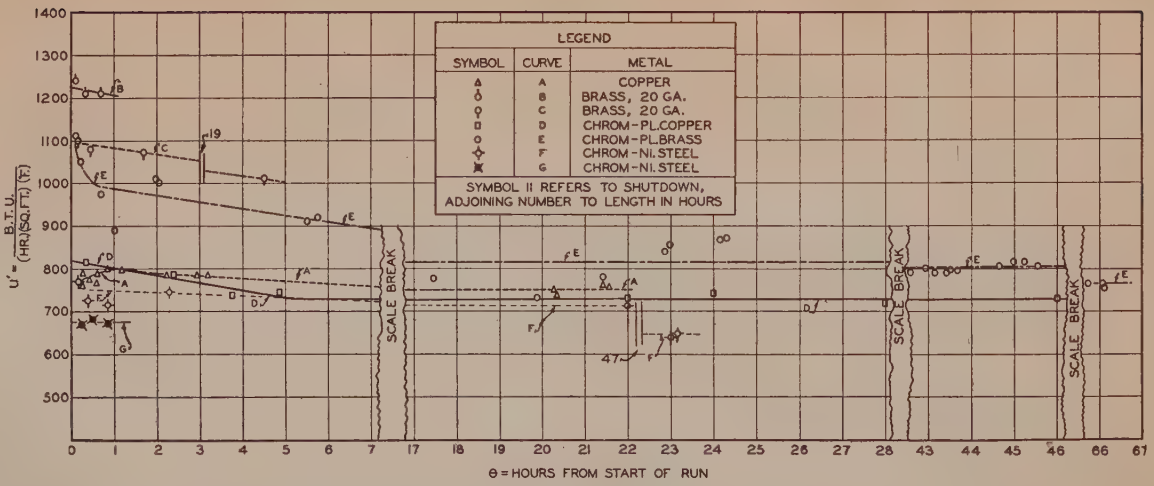
LEGEND
SYMBOL | CURVE | METAL
A | COPPER
B | BRASS, 20 GA.
C | BRASS, 20 GA.
D | CHROM-PL.COPPER
E | CHROM-PL.BRASS
F | CHROM-NI. STEEL
G | CHROM-NI. STEEL
SYMBOL II REFERS TO SHUTDOWN, ADJOINING NUMBER TO LENGTH IN HOURS
U = B.T.U. / (HR.)(SQ.FT.)(°F.)
θ = HOURS FROM START OF RUN
SCALE BREAK
SCALE BREAK
SCALE BREAK

FIG. 11. Overall coefficients of heat transfer for drop-wise condensation: smooth surfaces of copper, brass, chromium-plated copper, chromium-plated brass, and chrome-nickel steel.

Curve *A*. Copper tube, buffed with Tripoli and wiped with "fuel oil" on cloth.

Curve *B*. 20-gage brass, cleaned with precipitated chalk and wiped with oleic acid on cloth.

Curve *C*. 20-gage brass, polished very smooth with rouge and oleic acid on a cloth and then rubbed with a clean cloth. Non-wettable to cold water. After the 19-hour shut-down mixed condensation obtained for a few minutes, followed however by complete drop-wise.

Curve *D*. Chromium-plated copper, washed with soap and water. There was a gradual decrease from 100% drop-wise condensation at the start to 90% after 46 hours of operation.

Curve *E*. Chromium-plated brass: Approximately 5% of the area gave film condensation at the end of the run.

Curve *F*. Chrome-nickel steel, ground smooth on speed lathe, buffed with emery and fat compound, and washed with soap and water. Non-wettable to cold water.

Curve *G*. Smooth chrome-nickel steel, polished with red oxide of iron in water and cleaned with precipitated chalk, then rubbed with oleic acid on a cloth.

Curve	*Water Rate* *lb./hr.*	*Inlet Temp.* *°F.*	*Heat Load* *B.t.u./(hr.)(sq. ft.)*
A	585—605	57—59	102000—112000
B	610—615	68	148000—152000
C	550—560	77	123000—126000
D	570—585	57—59	100000—112000
E	555—595	55—57	117000—154000
F	565—595	64—67	74000—78000
G	570—580	67	69000—70000

Roughness was in general unfavorable to drop-wise condensation. Both copper and brass, roughened with coarse emery cloth and coated with oil or fat, gave film condensation even though the surface would not wet with cold water. However, both copper and brass gave drop-wise condensation when the surface had been made moderately rough by scouring, first with water and No. 180 emery, and then with oleic acid and the same abrasive.

Nickel.—The surface of the nickel tube as received was very rough, due apparently to grinding on a coarse emery wheel. The influence of roughness in preventing drop-wise condensation, even when the surface was treated with oleic acid, was apparent from the series of runs on this tube. After the tube had been cleaned with precipitated chalk and rubbed with a rag containing a very small amount of oleic acid, the heat transfer test showed some sluggish drop-wise condensation at first, but 100% film condensation after 5 minutes. After an overnight shut-down the same tube was tested again, without having been touched. Except at the very start of the run, no drops formed. The run lasted three hours. The tube was then made somewhat smoother by scouring the surface with No. 180 emery on a wet cloth, then coated with a thin film of oleic acid by rubbing with No. 180 emery on a cloth containing a little oleic acid. The emery and excess fat were then wiped off with a dry paper towel. To cold water the tube was sluggishly drop-wise. During the heat transfer run, the tube gave 100% drop-wise condensation near the start, 75% drop-wise after 20 minutes, and 60% drop-wise after 75 minutes. After scouring the tube again for a long time with No. 180 emery on a wet cloth, and rubbing it with No. 180 emery on a cloth moistened with a little oleic acid, the surface was very much smoother. The tube was then wiped with a clean dry cloth, and was found to be non-wettable to cold water. In the heat transfer apparatus, the condensation was 100% drop-wise throughout a run lasting over two hours. After an overnight shut-down the tube was again found to give 100% drop-wise condensation during a 25 minute run. The tube was next made even smoother by using various grades of emery on wet cloth and treated again with oleic acid. During 7½ hours of operation, interrupted by two periods of shut-down, the condensation obtained was 95% to 100% drop-wise, see curve A, Fig. 12.

Several runs were also made on cleaned nickel. These runs were made after the surface had been smoothed with emery flour as de-

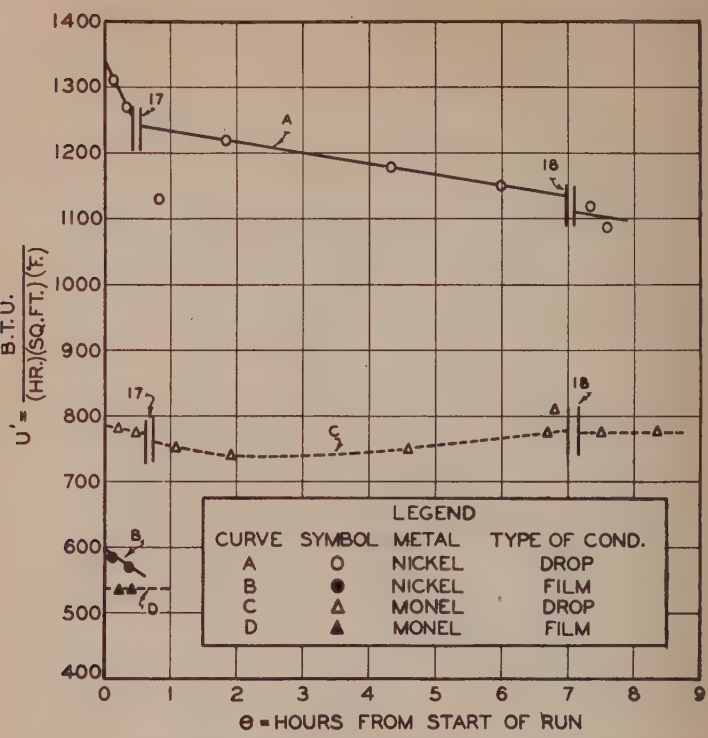

Fig. 12. Overall coefficients of heat transfer for film and drop-wise condensation: nickel and monel metal.

Curves *B* and *D*. Film condensation on surfaces scoured and roughened with No. 80 emery and water. Scoured surfaces were wettable to cold water.

Curves *A* and *C*. Drop-wise condensation on surfaces ground smooth by using No. 80 emery, No. 180 emery, and FFF emery flour in succession. Surfaces were then wettable to cold water. Next oleic acid was applied with emery flour on a cloth and the surfaces were washed with soap and water. After the oleic acid treatment the surfaces were non-wettable.

Curve	*Water Rate lb./hr.*	*Inlet Temp. °F.*	*Heat Load B.t.u./(hr.)(sq.ft.)*
A	510—560	75—76	121000—141000
B	550—585	75	70000— 72000
C	535—585	75	79000— 84000
D	550	76	60500

scribed in the preceding paragraph. Before each run the tube surface was freshly cleaned by using emery flour, followed by precipitated chalk on a wet cloth. After such treatment cold water wet the surface readily. Although the behavior of the tube was far from uniform in all runs, the tendency to change from film condensation at the start to drop-wise after considerable length of run was apparent (see Fig. 13). In one run the type of condensation changed from 100% film

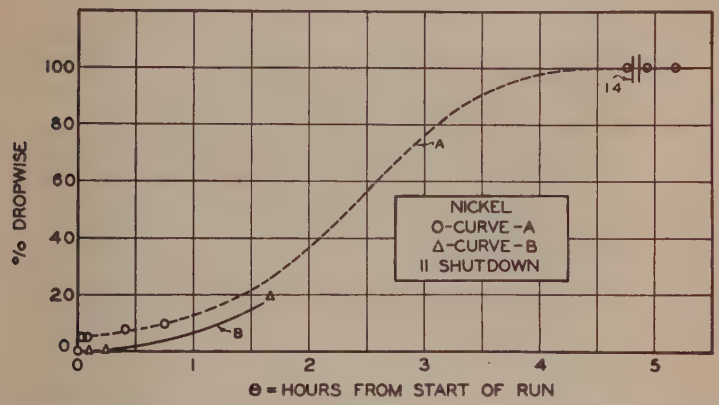

FIG. 13. Change of type of condensation with time: cleaned, fairly smooth nickel.

Curve *A*. Tube surface scoured with FFF emery flour on wet felt and cleaned with precipitated chalk. Completely wettable to cold water. However, at the end of the run tube was removed and found non-wettable.

Curve *B*. Surface cleaned before the run in the same manner.

to 100% drop-wise in approximately five hours. The per cent drop-wise condensation did not become less during periods of shutdown. Before one run, curve B, Fig. 12, the surface was roughened with No. 80 emery. In this run only a few drops were visible at the end of 2½ hours of operation.

Monel Metal.—The surface of the new monel metal tube was quite smooth. Treatment with oleic acid gave fairly good drop-wise condensation. Even when oleic acid was applied with No. 180 emery, which left a slightly rough surface, approximately 99% drop-wise condensation resulted. In a later run on a smooth surface treated with oleic acid 100% drop-wise condensation resulted, even after 8 hours operation and two overnight shut-downs, curve C, Fig. 12.

The behavior of condensing steam on a smooth cleaned surface of monel metal was similar to that in many runs on smooth cleaned copper and brass. As may be seen from Fig. 14, the percentage of drop-wise condensation increased with time, after a decrease during the first few minutes. Some evidence was obtained that monel metal, like copper and brass, may give less drop-wise condensation just after a period of shut-down than immediately before. In a later run, the surface was roughened with No. 80 emery on a wet cloth, after which

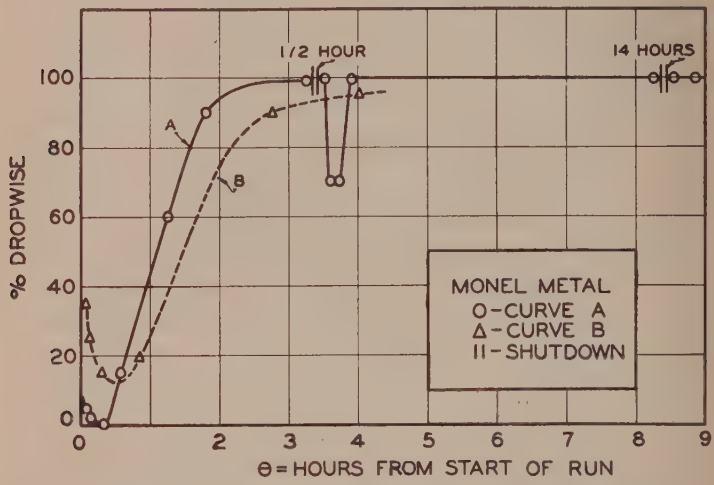

FIG. 14. Change of type of condensation with time: cleaned, fairly smooth monel metal.

Curve *A*. Tube surface scoured with FFF emery flour on wet felt and cleaned with precipitated chalk. Completely wettable to cold water. After the run the tube was found non-wettable.

Curve *B*. Surface cleaned in same manner.

the tube maintained film condensation throughout a 30 minute run when some heat transfer data were obtained (Curve *D*, Fig. 12).

Steel.—No satisfactory drop-wise condensation was obtained with steel tubes, even after the surface was made smooth by buffing and given a film of oil. Rapid corrosion, leaving a rough pitted surface covered by wettable oxides of iron, left little hope of obtaining good drop-wise condensation on this metal.

Aluminum.—Aluminum also proved unsuited for drop-wise condensation. On the surface in contact with steam, a thin adherent

scale formed which was mat-gray in appearance and very difficult to remove. This thin film of scale wet readily with water.

Beeswax and oleic acid were rubbed on the smooth aluminum tube, but both failed to produce a drop-wise condensation lasting more than a few minutes. Although the fat-treated tube was non-wettable in water before each run, it was perfectly wettable afterward.

One run was made with a surface that had been cleaned with emery flour. The condensation was completely of the film type for the entire run of six hours, interrupted by two periods of shut-down. Data for this run are given as Curve *A*, Fig. 15.

Chromium Plate.—It was found very difficult to obtain film condensation on chromium-plated copper and on chromium-plated brass. The tube of chromium-plated brass wet with cold water after it had been soaked one-half hour in a solution of hot caustic. In the condenser, the tube gave film condensation at first, 30% drop-wise after one-half hour, and 95% after 5 hours and until shut-down 20 hours after the start. After soaking the tube of chromium-plated copper in a solution of hot caustic for two and a half hours, immersion in cold water left an unstable film on the surface. When the tube was inserted in the condenser it was found that the condensation was 70% drop-wise and 30% film for an hour. Thereafter, the drop-wise area began to increase, reaching 100% after five hours. After cleaning the tube with "Wet-me-Wet," * cold water left an almost complete film, and a condensation test gave 30% drop-wise at start and 60% drop-wise after one and a half hours. After cleaning the surface by polishing with red oxide of iron on a wet cloth followed by precipitated chalk on a wet cloth, the surface was wettable with cold water, and, during a heat transfer run lasting twenty minutes, only 15% of the area gave drop-wise condensation. Immediately after shut-down on the run just mentioned, the chromium-plated copper tube was removed, wiped dry, wiped with a cloth containing a little oleic acid, and started up again in the condenser. Then it gave beautiful drop-wise condensation throughout a two-hour run. However, treatment with fat was not found necessary to obtain drop-wise condensation on chromium plate. Figure 10b shows drop-wise condensation on chromium plated copper.

One run on chromium-plated copper lasting approximately 46 hours, with one period of shut-down, and one run on chromium-plated brass lasting 68 hours are plotted as curves *D* and *E* in Fig. 11.

* A commercial window-cleaning compound.

A strange behavior of the chromium-plated copper tube was noticed. On two separate occasions, considerable (up to 70%) film condensation was observed after the tube has been smeared with a coat of "fuel oil." It is believed that an emulsion formed on the surface and retarded drop formation. However, subsequent attempts to repeat this result failed; and complete, or nearly complete, drop-wise condensation followed application of a film of "fuel oil."

Chrome-Nickel Steel.—This metal was found well suited for the study of film and drop-wise condensation, since it was not corroded by steam. Runs made after cleaning the tube gave little or no drop-wise condensation. Data on four runs on chrome-nickel steel cleaned in various ways are given as curves B, C, D and E of Fig. 15. Both rough and smooth surfaces are represented. Other runs, in which no heat transfer data were obtained, gave nearly perfect film condensation on smooth chrome-nickel steel which had been cleaned with precipitated chalk or "Wet-me-Wet."

The tube with its original very rough surface gave complete film condensation throughout a 46-hour run, even after it was wiped with a cloth dipped in "fuel oil." However, after the surface had been ground smooth and buffed with a commercial emery abrasive containing a fatty binder, complete drop-wise condensation resulted, and lasted for twenty hours (curve F, Fig. 11). The fatty film was removed with hot caustic solution, and several runs were made to test the effect of wiping the surface with an oily cloth. In no case was satisfactory drop-wise condensation obtained. "Fuel oil" and Russian mineral oil gave mixed condensation every time. Even soap was found to promote mixed condensation for a short time. Kerosene was used before one run and was found to give no drop-wise condensation. Olive oil and mutton tallow gave mixed condensation. Beeswax and stearic acid were much better. A commercial polishing compound containing Tripoli and a fatty binder, whether applied on a buffing wheel or by hand, was found quite good for promoting drop-wise condensation. Figure 10c is a photograph of drop-wise condensation on chrome-nickel steel. Oleic acid, however, seemed to be the best of all the substances tried, although a strict comparison is difficult to make due to the influence of roughness and of the method of application. Even oleic acid did not invariably give 100% drop-wise condensation. The effect of this substance seemed to be increased when it was applied with a soft abrasive.

With one exception, there was no decrease in per cent drop-wise condensation during periods of shut-down. The per cent drop-wise area did not increase with time; in many runs a gradual decrease was noted.

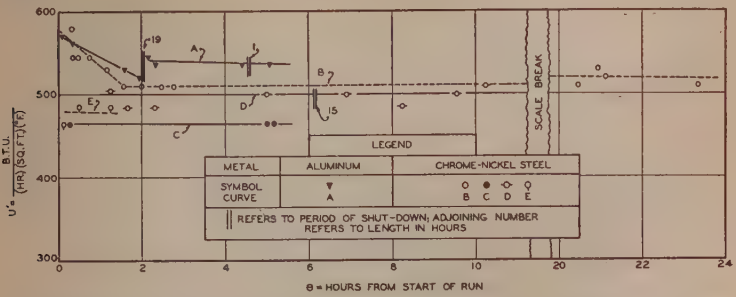

FIG. 15. Overall coefficients of heat transfer: film condensation on tubes of aluminum and chrome-nickel steel.

Curve *A*. Aluminum tube, scoured with FFF emery flour and water. Wettable to cold water.

Curve *B*. Chrome-nickel steel tube, as received with very rough surface. Was cleaned with "Gresolvent" and water until wettable. During the run the condensate film was irregular, approximately 1% of the surface appearing dry.

Curve *C*. Above tube, ground smooth on a speed lathe and buffed with emery buffing compound, then soaked 20 minutes in hot caustic. During the first 5 hours of the run approximately 5% of the surface was covered by "dry" spots which later changed to spots of drop-wise condensation. Was incompletely wettable before the run.

Curve *D*. Above tube again ground and buffed with emery and Tripoli buffing compounds, then cleaned with precipitated chalk. Incompletely wettable to cold water. For the 6 hours of operation before shut-down the condensation was in the form of an irregular film; for the period after shut-down 5% of the area gave drop-wise condensation.

Curve *E*. Same tube, polished with red oxide of iron on wet cloth and cleaned with precipitated chalk. Gave complete film condensation except for a few small "dry" spots.

Curve	*Water Rate lb./hr.*	*Inlet Temp. °F.*	*Heat Load B.t.u./(hr.)(sq.ft.)*
A	565—615	76—77	65000—71000
B	575—610	58—60	59000—66000
C	555—605	66—67	53000—53500
D	585—655	68—69	54000—56000
E	565—570	67	53000—54500

Résumé of Heat Transfer Data.—Corrected overall coefficients * of heat transfer, U', obtained in the small condenser on tubes of aluminum, brass, copper, monel metal, nickel, and chrome-nickel steel, all

* $\frac{1}{U'} = \frac{1}{U} - \frac{L}{k}$.

giving film condensation, averaged 500 B.t.u./(hr.)(sq.ft.)(° F.) with a variation of approximately 10%.

The coefficients, U′, obtained on tubes of copper, brass, chrome-nickel steel, chromium-plated copper, chromium plated brass, monel metal, and nickel, giving drop-wise condensation, varied from 600 to 1300 B.t.u./(hr.)(sq.ft.)(° F.). Lack of better agreement among different tubes giving drop-wise condensation may be due, in part, to the values used in correcting for the resistance of the tube wall. How-

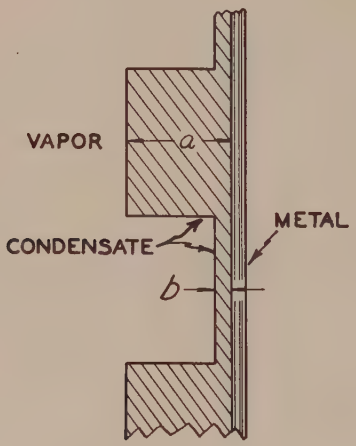

FIGURE 16

ever, in drop-wise condensation, the size of the drops and the apparent ease with which they detach themselves from the tube surface, varied among different runs. A corresponding variation in the heat transfer coefficient is to be expected and may help to explain the discrepancies found for this kind of condensation.

THEORETICAL DISCUSSION

In most of the original papers dealing with drop-wise condensation no intelligible explanation has been given of the fact that this mode of condensation has an individual coefficient much higher than that for condensation in a film. Such an explanation is found in a method of reasoning used by Ginabat [9] in 1924 and summarized by Wulfinghoff [19] in 1933.

Suppose a layer of condensate on a cooling surface take the form shown in Fig. 16, and let one of the two adjacent spots of equal area A be covered by a thickness, a, of condensate, and the other by a smaller thickness, b. Let Q_a be the heat current through the layer of thickness a; and Q_b that through the layer of thickness b.

If the temperatures of the steam and of the cooling surface are substantially uniform, $Q_a = k' A \triangle t/a$ and $Q_b = k' A \triangle t/b$, where k' is the thermal conductivity of the condensate, and $\triangle t$ the temperature drop from the vapor to the cooling surface.

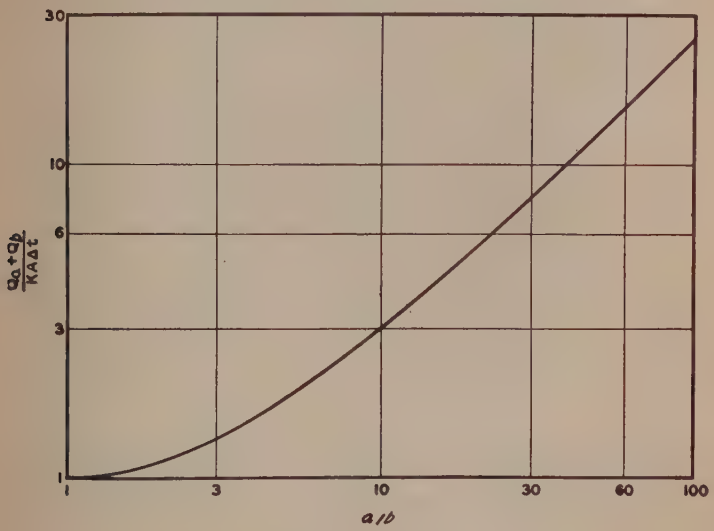

FIGURE 17

Consider how, with a constant average weight of adhering condensate per unit area, the ratio a/b affects the average rate of heat flow through the layer of condensate. For the sake of illustration, let $a + b = 4$. The amount of heat transferred through the two adjoining spots when $a = b$ is

$$Q_a + Q_b = k'A \triangle t(1/a + 1/b) = k'A \triangle t \ (\tfrac{1}{2} + \tfrac{1}{2}) = k'A \triangle t.$$

The increase of heat transferred as the ratio a/b changes is given in Fig. 17. In film condensation, adjacent spots have nearly the same film thickness, or in the hypothetical case above, $a = b$. In drop-wise

condensation the thickness of a drop is many times the thickness of the condensate layer between drops. Hence the coefficient of heat transfer for drop-wise condensation should be markedly higher than that for film condensation, if the amount of condensate held on the cooling surface is no greater for drop-wise than for film condensation. Data are at present unavailable for determining the relative amounts of holdup for the two modes of condensation.

When a vapor condenses on a solid surface, the entire surface is undoubtedly covered by condensate. Whether the condensate on the surface draws together as tiny droplets or grows into a uniform film of appreciable thickness should depend to a large extent on the molecular forces of attraction between two liquid molecules and between a liquid and a solid molecule. If the force of cohesion between liquid molecules is sufficiently large and the force of adhesion

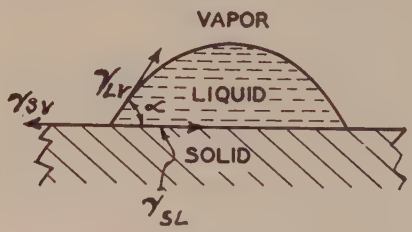

FIGURE 18

between liquid and solid is sufficiently small, the liquid will be unstable as a film and should form drops. The forces acting on a drop of liquid on a flat solid surface (Fig. 18) may be represented by the interfacial tensions γ_{SV}, γ_{SL}, and γ_{LV}, where S, L and V refer to solid, liquid, and vapor, respectively, so that the double subscripts indicate the interface referred to. At equilibrium $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \alpha$.

If $\gamma_{SV} > \gamma_{SL} + \gamma_{LV} \cos \alpha$, the drop will tend to spread and cover a larger area, but if $\gamma_{SV} < \gamma_{SL} + \gamma_{LV} \cos \alpha$, the drop will tend to become more spherical and cover a smaller area of the solid.* Hence, Buckley and Snyder [5] for example, have used, $\gamma_{SV} - \gamma_{SL} - \gamma_{LV}$ as a measure of the tendency of a drop of liquid to spread on the surface of a solid. Analogously the tendency toward the formation of a spherical drop might be supposed to be measured by $Z = \gamma_{SL} + \gamma_{LV} - \gamma_{SV}$. If so, drop-wise condensation of a vapor should be favored

* Cf. Eucken, Jette, and LaMer [6]; Adam [1]; and Young.[20]

by a high surface tension of the condensate, a high interfacial tension between solid and liquid, and a low interfacial tension between solid and vapor. Admittedly it may be dangerous to make predictions concerning condensation from an expression such as $\gamma_{SL} + \gamma_{LV} - \gamma_{SV}$ evaluated by isothermal data. However, even with these data, some insight into the problem may be had by consideration of the interfacial forces. For example, such substances as mercury, water, glycerine, and aniline, which have a high surface tension, should have a tendency towards drop-wise condensation, other things being equal.

An interesting observation on the effect of interfacial tensions was made in a number of cases of mixed condensation. Drops sliding down the tube are attracted markedly if they pass close to a spot giving film condensation. Drops formed within approximately ¼ inch below such a film spot may even be drawn upward into that spot.

From the well known laws of interfacial adsorption, it is apparent that it is easy to lower the surface tension of a liquid by adding a small amount of a suitable substance although to increase the surface tension materially by a similar small addition is impossible. Hence, if there is no choice of vapor to be condensed, there is little that can be done to produce a high value of γ_{LV}. Therefore, from a practical point of view, the problem of varying the type of condensation, considered as equivalent to that of varying Z, reduces to the problem of changing the difference $\gamma_{SL} - \gamma_{SV}$. This quantity is readily altered by surface treatment * and contamination.

A clean, fat-free, glass surface is completely wettable with water; this forms the standard test for cleanliness in the analytical laboratory. Complete wettability with water is used by electroplaters as the criterion of cleanliness for all metal surfaces. All fresh, highly polished metal surfaces are found to be completely wettable with water if the polishing powder was used in water suspension and was fat-free.[10] In other words, $\gamma_{SL} - \gamma_{SV}$ is very small for water on clean metal. This complete wettability would lead one to expect film condensation on all clean metal surfaces. In general, this expectation was realized. Such cleanliness is, however, difficult to maintain. If the metal is standing in air for a short time, complete wettability may be lost. Contamination by foreign matter or products of corrosion may destroy the wettability. Such contamination is probably to blame for the difficulty experienced in maintaining complete film condensation on

* Beilby [2] discusses the effect of polishing on surface energy.

smooth surfaces. Frequently when mixed condensation had developed on supposedly clean surfaces, at the end of the run the film areas were wettable with cold water, while the drop-wise areas were not.

It is well known that greasy surfaces of all sorts are not readily wetted by water. Thus, the difference $\gamma_{SL} - \gamma_{SV}$, and hence Z, for water on the surface of a solid is increased by contaminating the surface with oil. Buckley and Snyder [5] have shown that the interfacial tension between metals and fatty oils or fatty acids is less than the interfacial tension between metals and water, which in turn is less than the interfacial tension between metals and petroleum oils. That is, fatty oils and fatty acids have a greater tendency to adhere to a metal surface than has water or mineral oil. This probably explains why oleic acid and other fatty materials are more effective than mineral oils for maintaining drop-wise condensation.

Experience gained from work on the flotation of minerals should be of help in the study of drop-wise condensation of steam. Sulfide minerals are less readily wet by water than oxide minerals. Hence one would expect that sulfide corrosion products on a metal surface might favor drop-wise condensation of steam while oxide corrosion products should hinder it. The effect of oxide corrosion products is illustrated by the fact that steel and aluminum give film condensation. In flotation practice, minerals are made less readily wettable by treatment with soaps, oleic acid and other fatty acids, xanthates, mercaptans, dithiophosphates, thiocarbanilid, etc. In the present investigation soap and fatty acids were tried and found to increase the tendency to drop-wise condensation.

Even when the conditions are favorable to drop-wise condensation the vapor might conceivably condense on the surface faster than the condensate film could break up into drops. In that case, the entire surface would be covered by an unstable film of liquid through which the heat must flow, and the coefficient of heat transfer would be the same as for film condensation with an equal steam rate. It has been frequently observed in this laboratory that a tube giving mixed condensation may be made to give complete drop-wise condensation by reducing the steam pressure slightly or by cutting off the supply of cooling water. However, the best surfaces for drop-wise condensation could be operated at steam condensation rates as high as 150 lbs./(hr.)(sq.ft.) with no film area whatever. Schmidt, Schurig, and Sellschopp [16] obtained even higher condensation rates with 100% drop-wise condensation.

A large number of experiments which have been performed in this laboratory and elsewhere exhibit film condensation on rough surfaces which contain a film of oil and are not wet with cold water. The roughness may mechanically delay the contraction of the condensate into drops. On a copper plate ground in one direction with coarse emery, a drop of mineral oil spreads more slowly across the scratches than it does along them. As spreading is delayed by a rough path, so may the contraction of a film into drops be delayed.

Work is being actively continued on the numerous doubtful points.

Acknowledgment

The authors are grateful to Prof. W. H. McAdams for his continued and enthusiastic support both in the experimental work and in the preparation of this paper, to Mr. L. Squires for his help in many of the phases of the problem which involved surface physics, and to Messrs. Billings and Wadt for their co-operation in obtaining a considerable part of the data presented here. They wish to express their thanks to Prof. J. J. Eames for making available the necessary laboratory facilities. Some of the tubes tested were furnished through the courtesy of the National Tube Company and the International Nickel Company. The pyrex cylinders which were vital to the success of the investigation were made available through the kind efforts of Dr. E. C. Sullivan.

Table of Nomenclature

A = area of heating surface,
a, b = thickness of layer of condensate,
h_s = individual coefficient of heat transfer, condensing steam to metal,
k = thermal conductivity of metal tube,
k' = thermal conductivity of condensate,
L = thickness of tube wall,
Q_a, Q_b = rate of heat flow through condensate layer of thickness a, and b respectively,
$\triangle t$ = temperature drop,
U = overall coefficient of heat transfer,
U' = corrected overall coefficient of heat transfer, defined by the equation: $1/U' = 1/U - L/k$,
U_c = overall coefficient for a cleaned tube,

U_D = overall coefficient for drop-wise condensation,
U_F = overall coefficient for film condensation,
U_f = overall coefficient for a fouled tube,
$Z = \gamma_{SL} + \gamma_{LV} - \gamma_{SV}$,
α = contact angle,
γ_{LV} = interfacial tension between liquid and vapor phases,
γ_{SL} = interfacial tension between solid and liquid phases,
γ_{SV} = interfacial tension between solid and vapor phases,
"% drop-wise" = per cent of the area of a tube over which drop-wise condensation is occurring.

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Note by the Authors

Experiments using tubes of copper and copper alloys conducted since this paper was written, have confirmed the prediction that a high effectiveness for the promotion of drop-wise condensation would be possessed by mercaptans, xanthates, and dithiophosphates. The use of these treating agents and of the higher fatty acids is described in a U. S. Patent application filed by W. M. Nagle.

It has also been shown that the development of sulfide corrosion films on brass condenser tubes will cause a change from film-forming

to drop-wise condensation. It is not impossible that the boiler steam used in some of the tests might have contained traces of sulfur, derived from gaskets, etc. This may explain some of the "change-overs" observed in the earlier experiments.

Discussion

(Summarized by T. H. Chilton, Chairman of the Sub-Committee on Papers)

The authors presented a motion picture illustrating the change from film to drop-wise condensation following the injection of a small quantity of oleic acid into the steam space of the experimental condenser described in the paper. W. L. Badger reported that a new copper tube was often found in his experiments to give erractic heat transfer coefficients and his practice was to steam the tubes for a week in order to secure reproducible results. T. H. Chilton pointed out that as a result of this paper it will hereafter be necessary to define much more accurately the nature of the condenser tube surface, and the quality of steam used especially as regards oil content, etc. D. F. Othmer reported that the injection of hydrochloric acid into the steam sufficed to give good heat transfer coefficients on a copper tube condenser; this appeared to remove a copper oxide film. He also pointed out that air-free steam was necessary to give the highest coefficient. T. B. Drew stated that a small amount of air appears to improve the coefficients by inducing drop-wise condensation under certain conditions, whereas, of course, a large amount of air reduced the coefficients as usual. A motion picture was presented representing the work of J. O. Jeffrey and J. R. Moynihan, obtained by the chairman, through the kindness of Prof. H. Diederichs. This illustrated the formation of drop-wise condensation on horizontal brass condenser tubes.

A STUDY OF ENTRAINMENT IN A FORCED CIRCULATION EVAPORATOR

By OREN C. CESSNA * and WALTER L. BADGER †

The purpose of this research was to study the entrainment of liquor by the vapor in an evaporator of the forced circulation type, and to determine the relation between the quantity of liquor carried by the vapor and the conditions maintained within the evaporator.

The small amount of work that has been done on the subject of entrainment has all pertained to steam boilers. A large part of this work has been done by Foulk who has also made a rather complete summary of what has been done by others [2]. Vorkauf [1] studied the subject rather comprehensively using small scale laboratory apparatus designed to give conditions similar to those in a steam boiler.

The work referred to above is of interest to this problem only inasmuch as it gives some insight into the mechanism of entrainment and advances some theories upon the formation and behavior of the droplets. The results obtained, however, are not directly applicable because the forced circulation evaporator is quite different, both in design and in operation.

More directly connected with evaporators is the study made by Hausbrand [3] in 1899. The discussion was entirely from a theoretical standpoint and was not supplemented by any direct experimental data. It deals with the effect of currents of vapor upon droplets of liquor under various circumstances, and gives equations expressing the relationship for each case.

Of the various cases that Hausbrand considered, one in which a vertical current of steam meets a drop of liquid thrown obliquely is quite similar to the present problem; and although he was mainly interested in the point at which entrainment begins rather than the amount of entrainment, his treatment of the problem might easily be modified to apply to this case.

Hausbrand found the following relationships,

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* The material in this paper forms a part of the dissertation submitted by Mr. Cessna for the degree Doctor of Philosophy at the University of Michigan.

† Dept. of Chemical Engineering, University of Michigan, Ann Arbor, Mich.

$$D = \psi \gamma_e Q \frac{v^2}{2g}$$

and,

$$\frac{D}{G} - 1 = \frac{2c}{gt}\left(\sin \alpha - \cos \alpha \tan \frac{\alpha}{2}\right)$$

In the above equations

D = pressure exerted upon the drop by the vapor
Q = the projected plane surface of the drop
γ_e = density of the vapor
v = relative velocity between the vapor and the drop
g = acceleration of gravity
ψ = a numerical coefficient
c = initial velocity of the drop
α = angle between the path of the drop and the horizontal
t = time the drop is in the vapor current before hitting the wall.
G = diameter of the drop.

These equations when combined yield a relationship very similar to that derived below.

General Discussion

Entrainment is entirely a mechanical process. A small portion of the liquor in the body of the evaporator is carried upward in the form of droplets by the vapor and passes into the condenser, resulting in a loss of the material contained within the machine and the contamination of the overhead condensate.

The process is, in general, made up of two parts: the formation of the droplets and the entraining of the droplets by the vapor. The manner in which these two steps take place depends to a great degree upon the type and design of the evaporator. The formation of droplets in a forced circulation evaporator is quite different than in a natural circulation evaporator or a steam boiler.

As a basis upon which to develop a theory for the process, consider the general principle upon which the forced circulation type operates. Referring to Figure 1, the main portion of the liquor being evaporated is contained in the body and surrounds but does not submerge the heating element *m*. The circulating pump *p* draws the liquor from the body through the downtake *n* and forces it through the control valve, the distributing box *o*, and the tubes *k*. Emerging from

the tubes at a rather high velocity the liquid strikes the deflector *j*, which changes its direction and throws it obliquely downward against the wall in a sheet, called the "curtain." Steam is supplied to the heating element and surrounds the tubes. Nearly all the vapor is formed in the upper part of the tubes, passes upward with the liquid and is released below the deflector. All the vapor formed must pass through the curtain into the vapor space and then out into the condenser.

Although small droplets will be ejected from the main body of the liquid by bubbles breaking and the vapor leaving the tubes will undoubtedly carry a mist with it, the chance that these particles can pass through the curtain without being swept down is small. It is obvious, therefore, that any entrained particles appearing in the vapor space must have come from the curtain itself. The curtain probably is not a solid mass of liquid, but consists of small drops varying in size, close together, and moving with considerable velocity. Assuming that the curtain remains unbroken, the vapor must pass between the particles and will carry some of them upward with it. The size of the particles picked up by the vapor will depend upon the direction and velocity in which the particles are travelling when they leave the deflector and the velocity of the vapor through the curtain.

Once the droplets of liquid have reached the vapor space their further progress will depend upon their size and the velocity of the vapor at this point. Only those particles that are sufficiently influenced by the vapor to overcome the force of gravity will proceed into the condenser; the remainder will fall back into the main body of the liquid. It is possible that when the curtain has a very low velocity, or is very thin, the conditions in the vapor space may control the amount of entrainment, but under the usual operating conditions it is more probable that the removal of droplets from the curtain controls throughout. This is because the velocity of the vapor through the curtain is usually less than in the space above, and that sufficient force is required to overcome the initial velocity of the drops as well as the effect of gravity.

The force exerted upon small solid particles by a stream of fluid has been determined and has been utilized in the development of hydraulic settling and air separation. The derivation of the equation is generally known and depends upon the fact that the frictional resistance between the fluid and the particle must be equal to or greater than the force of gravity [4]. The same line of reasoning can be

applied in the development of the relationship between the factors controlling the amount of entrainment in a forced circulation evaporator; that is, the force upon the droplets due to friction must be equal to that necessary to cause them to leave the curtain and travel upward.

In order to obtain this relationship it is necessary to make three general assumptions.

1. The curtain is circumferentially uniform in thickness.
2. If the vapor passes through the curtain in a curved path or if all the vapor in any vertical diametral plane is not travelling in the same direction, the net effect will be the same as though the vapor were following parallel lines making a certain angle with the horizontal.
3. Those particles that are sufficiently deflected from their path to travel upward and pass the tip of the deflector inside a certain point will be carried into the vapor space, while those passing outside this point will strike the wall of the evaporator. The point defined is, therefore, the point through which the largest particles to be carried over will pass and is at a certain fraction of the distance between the deflector and the wall. This fraction is unknown but is assumed to be constant for a given evaporator.

Notwithstanding these simplifying assumptions, the relationship between some of the factors is quite involved and it is necessary to neglect their effect in order to avoid a complicated and practically useless equation. It should be understood, therefore, that the expression derived is not entirely rigorous and is not presented as an exact theoretical equation. This derivation is merely a line of reasoning based upon various logical assumptions and was undertaken to ascertain the various factors that influence the amount of entrainment and to determine, if possible, the manner in which these factors should be grouped in the equation.

Referring to Figure 4, a cross-sectional diagram of the curtain and the forces upon it is shown. On the space diagram the line $\overline{WX}$ is the tip of the deflector making an angle α with the horizontal line $\overline{XO}$. $\overline{OL}$ is the wall of the evaporator at a distance S from $\overline{X}$. $\overline{XL}$ denotes the path of the curtain if free from accelerating effects. The point M is that point at which the largest particles to be carried over will pass the horizontal. All the particles passing to the left of this point will travel up into the vapor space, while those passing to the right of M will strike the wall.

The forces acting upon each droplet are those of gravity, F_g, acting downward and friction from the vapor, F_v, acting at an angle β with the vertical. The resultant of the two forces is the accelerating force, F_a, at an angle γ with the vertical. In comparison with the accelerating force, the force of gravity will be very small and will be neglected in this derivation, so that the force exerted by the vapor will be considered to be equal to the accelerating force acting at an angle γ with the vertical.

The motion of a droplet following the resultant (not actual) path $\overline{XM}$ can be divided into components, $\overline{XZ}$ in the direction of the original velocity and $\overline{ZM}$ in the direction of the accelerating force; or, briefly, the accelerating force, F_a, must be sufficient to cause the drop to move through the distance $\overline{ZM}$ in the time it would have traveled from X to Z if not so affected.

If C is the original velocity, and t the time for passing from X to Z,

$$t = \frac{\overline{XZ}}{C}$$

and the acceleration required is

$$a = \frac{2C^2\overline{ZM}}{\overline{XZ}^2}$$

The mass of the droplet is $\frac{A\rho' D^3}{g}$

Therefore

$$F_a = \frac{2A\rho' D^3 C^2 \overline{ZM}}{g\overline{XZ}^2}$$

Since $\overline{OX}$ equals s and $\overline{XM}$ is defined as $f(OX)$

$$\overline{XM} = f(s)$$

and

$$\overline{YM} = f(s) \sin \alpha$$

The angle $(\phi + \theta) = (\gamma - 90)$

$$\phi = (90 - \alpha)$$

and

$$\theta = (\gamma - 90) - (90 - \alpha) = (\alpha + \gamma - 180)$$

Then,

$$\overline{ZM} = \frac{\overline{YM}}{\cos(\alpha + \gamma - 180)}$$

$$= \frac{f(s)\sin\alpha}{-\cos(\alpha + \gamma)}$$

$$\overline{XZ} = \overline{XY} + \overline{YZ}$$

$$\overline{XZ} = f(s)\cos\alpha + f(s)\ [\sin\alpha\tan(\alpha + \gamma)]$$

$$= f(s)\ [\cos\alpha + \sin\alpha\tan\ (\alpha + \gamma)]$$

Substituting above,

$$F_a = \frac{2A\rho' D^3 C^2(\sin\alpha)}{gf(s)\ [-\cos(\alpha + \gamma)]\ [\cos\alpha + \sin\alpha\tan(\alpha + \gamma)]^2}$$

For any given evaporator, α, γ, s, and $f(s)$ are assumed to be constant.

$$F_a = R\rho' D^3 C^2$$

$$R = \text{a constant}$$

Since F_g is neglected and F_v equals F_a

$$F_v = R\rho' D^3 C^2$$

The expression for the force due to friction between a particle and a fluid is, [4]

$$F = \frac{\psi D^2 u^2 \rho}{g}\ \phi\left(\frac{D' u\rho}{z}\right)$$

In this expression u is defined as the velocity of the fluid relative to the particle. Although the droplets being considered here are in motion, the direction of that motion is nearly at right angles with that of the vapor and under the assumptions made above would not affect the force exerted by the vapor in the direction of acceleration.

The velocity of the vapor through the curtain, u_v, is, therefore, substituted for u.

Setting the expressions for the forces equal gives the equation,

$$\frac{\psi D^2 u_v^2}{g} \phi\left(\frac{D'u\rho}{z}\right) = R\rho' D^3 C^2$$

Solving for D,

$$D = \frac{\psi u_v^2 \rho \phi\left(\frac{D'u\rho}{z}\right)}{gR\rho' C^2}$$

The droplets carried by the vapor will range in diameter from D, the diameter of the largest, to zero. The number of drops of each diameter will undoubtedly follow some function of the probability curve and will change with the densities of the vapor and liquid. The volume of liquid carried per cubic foot of vapor will, therefore, be some function of D, ρ and ρ'. At the present time it is impossible to determine the nature of this function without considerable study outside the scope of the present problem. It has been assumed, therefore, that it can be empirically expressed as,

$$V_L = b\left(\frac{\rho}{\rho'}\right)^{\delta} \lambda(D)$$

where,

V_L = Volume of liquid per million cu.ft. of vapor.
b = an unknown constant,
δ = an unknown power
$\lambda(D)$ = an unknown function of D.

If E equals the pounds of liquid carried per million pounds of vapor, then

$$E = \frac{b\rho' \rho^{\delta} \lambda(D)}{\rho \rho'^{\delta}}$$

Substituting for D

$$E = \frac{b\rho^{\delta-1}}{\rho'^{\delta-1}} \cdot \lambda\left[\frac{\psi u_v^2 \rho \phi\left(\frac{D'u\rho}{z}\right)}{gR\rho' C^2}\right]$$

In the range covered $\phi\left(\frac{D'u\rho}{z}\right)$ will be practically constant;

and since ρ is very small in comparison with ρ' it may be assumed that $(\rho'-\rho) = \rho'$.
Then including b and ψ in the λ' function,

$$E = \frac{(\rho)^{\delta-1}}{(\rho')^{\delta-1}} \lambda' \left(\frac{\rho u_v^2}{\rho' C^2} \right)$$

Experimental Work

The data for the study of this problem were obtained upon an experimental, small-tube, forced-circulation evaporator. The general method used to determine the amount of liquid carried with the vapor was as follows. A solution of sodium chloride, approrimately 10 per cent by weight was placed in the body of the evaporator and distilled water was added continuously to replace that which was evaporated and thus maintain a constant concentration. The overhead condensate and the solution in the evaporator were analyzed and from their relative concentrations the pounds of liquid carried per million pounds of vapor was calculated.

The general construction of the apparatus is shown in Figure 1. It consisted of the evaporator equipped with all the necessary accessories, such as the circulating pump *p*, surface condenser *l*, vacuum pump *r*, manometer tubes *q*, and calibrated tanks *s* and *t* for the steam and overhead condensate. It is essentially standard in design so only those parts which are involved in the taking of data for this research will be discussed more fully.

The heating element is a double walled, plate-steel cylinder, eighteen inches in diameter, with sil-o-cel packed in the annular space. The tube sheets are ¾ inch thick and are eight feet apart. The heating surface consists of 30—½ inch O.D. 20 gauge copper tubes giving an area of 27.02 sq.ft.

Steam is introduced into the heating element at the center of the top tube sheet, and the condensate is removed at a point near the circumference of the bottom tube sheet. The vent can be connected to the atmosphere or to the vacuum pump as desired.

Mercury manometers are used to measure steam pressure, vacuum, pressure drop across the tubes, and pressure drop across an orifice in the circulation line.

Since the main condenser has a rather large surface and retains a considerable amount of liquid, the change in the concentration of the liquid leaving is gradual so that an appreciable time is required

to reach equilibrium after changing conditions. In order to expedite the taking of data, the accessory apparatus shown in Figure 2 was installed. *a* is the horizontal section of the 6 inch vapor line between the top of the evaporator and the condenser. The 1 inch pipe *b* was welded into the bottom of *a* and projects far enough inside so that

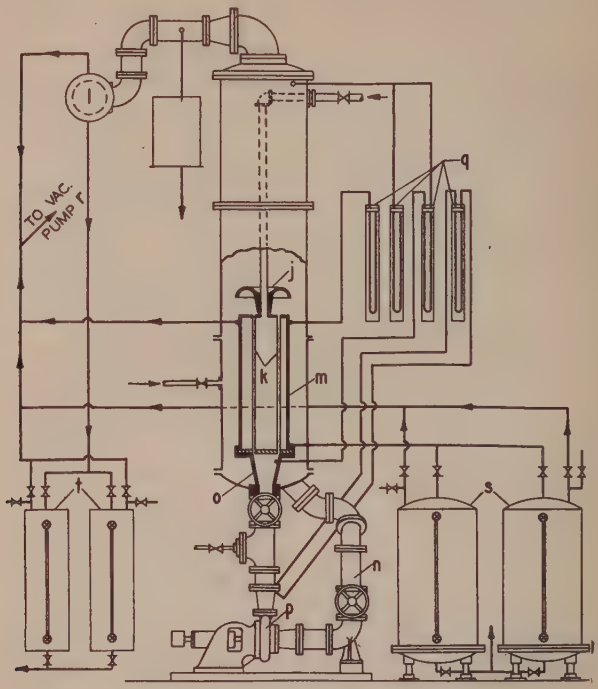

Fig. 1. Experimental Evaporator.

the short nipple *c* is directly in the center of *a*. The pipe *b* is connected to the auxiliary condenser *d* by a horizontal 1 inch pipe.

The auxiliary condenser *d* is made up of a ¾ inch copper coil submerged in a steel tank filled with water. The water is maintained at such a level that approximately 15 feet of the coil is submerged. The necessary heating surface was determined to be such that the effective area has the same relationship to the area of the main condenser that the cross-sectional area of pipe *c* has to the cross-sectional area of the annular space between *c* and *a*. Assuming that

the product of the overall heat transfer coefficient and the temperature drop is approximately the same in the main and auxiliary condensers, such a quantity of vapor will be condensed in condenser *d* that the velocity of the vapor through the pipe *c* will be the same as

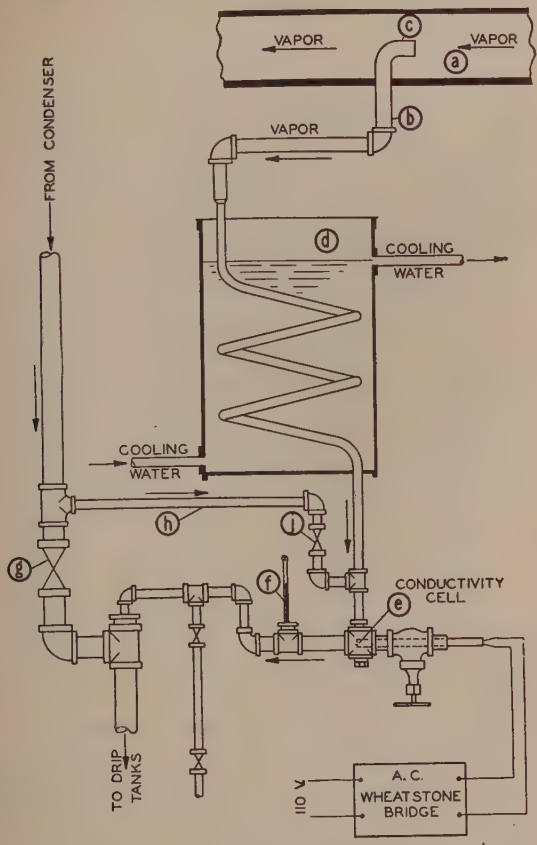

FIG. 2. Apparatus for Analysis of Overhead Drips.

the mean velocity through the annular space. In this way excessive turbulence at this point and the loss of entrained particles is avoided.

The condensate formed in condenser *d* runs directly down into a small trap and passes the conductivity cell *e* inserted in the side arm of a cross. The liquid comes into contact with the thermometer *f*

placed in a tee in the bottom of the trap and then leaves the trap, dropping into the top of a tee in the discharge line from the main condenser.

By partially closing the valve *g* in the main condensate line and opening the valve *i*, it is possible to run a portion of the condensate from the main condenser through the pipe *h* to the trap whenever desired.

In the preliminary runs the use of this by-pass showed that after the period of lag the condensate from the two condensers was of

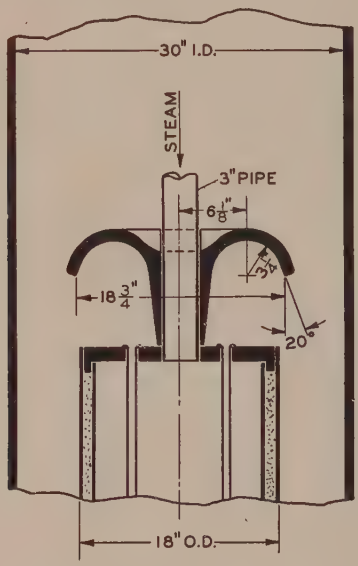

FIG. 3 Detail of Deflector and Curtain.

approximately the same composition. However, to insure that the data taken were representative, the auxiliary condenser was used only at the start of the run until equilibrium had been reached in the main condenser, and then the by-pass was opened and liquid from the main condenser used during the remainder of the run.

As was stated above the amount of entrainment was determined from the relation between the concentration of sodium chloride in the body of the evaporator and in the overhead condensate. The concentration of the solution within the evaporator was determined by

titrating with standard silver nitrate, using potassium chromate as an indicator.

The overhead condensate was analysed by a Leeds and Northrup conductivity cell. This was calibrated against salt solutions of known concentration over the range from 1 to 100 parts per million of sodium chloride, and at temperature intervals of 5°C.

Successive runs, twenty minutes in length, were made under each set of conditions until a check was obtained (usually two were sufficient). The level of the liquid in the steam and overhead condensate tanks was read at the start and at the end of each run; and ten readings, at intervals of two minutes, were taken on the four manometers, the Wheatstone bridge, and the thermometer in the trap. Qualitative notes were also made upon the condition of the curtain and the vertical distance from the tip of the deflector to the point the curtain met the wall, was measured. These measurements were approximate because the sight glasses were some distance apart and it was therefore necessary to estimate the lower point.

Between periods of operation there was a considerable change in the sodium chloride concentration in the body due to loss of the liquor, but while the evaporator was running the change was very small. A sample of the liquor was removed for analysis at the beginning and end of each run. Since they were of approximately the same concentration, the average of the two was used in the calculation of all the runs made during the period.

Correlation of the Data

The data obtained during the runs had to be converted into a form in which they could be correlated. The principal items desired for this study were E, the entrainment; u_v, the velocity of the vapor through hte curtain; u_L, the velocity of the liquid through the tubes; ρ, the density of the vapor; and ρ', the density of the liquid.

The difference between the saturation temperatures of steam and vapor, calculated from the manometer readings, was taken as the temperature drop through the heating surface. Since there was a boiling point rise due to the presence of sodium chloride in the liquor, this is the apparent rather than the true temperature drop.

The readings on the Wheatstone bridge and the thermometer could not, of course, be averaged directly. Instead, the concentration of the condensate in parts per million at the time of each reading was

taken from the calibration curves and the ten concentrations were averaged to obtained a value representative of the entire run. If the average concentrations of the condensate and of the liquor are known, then

$$E = \frac{(\text{Conc. of condensate})\ 100}{\text{Conc. of liquor}}$$

The vapor velocity, u, could be determined from the amount of liquid collected in the overhead condensate tanks during the run. Expressed algebraically,

$$u_v = \frac{(\triangle d)(W)(v_v)}{(20)(60)A_c}$$

where $\triangle d$ = Difference in level of overhead condensate, mm.; W = Calibration factor of tank, lb./mm.; v_v = Specific volume of vapor, cu.ft./lb.; A_c = Area of curtain, sq.ft.

In calculating the area of the curtain to be used in this equation the effect of gravity was neglected and the curtain assumed to be straight rather than parabolic in shape. In each case the area was determined from the observed length.

Since the pressure difference across the orifice as indicated by the ten manometer readings varied only slightly, the readings could be averaged directly and the corresponding liquor velocity through the tubes, u_L, determined from the calibration curve. The density of the vapor, ρ, is the reciprocal of the specific volume used in the calculation of vapor velocity, and that of the liquor, ρ', was obtained from the International Critical Tables giving the density of sodium chloride at various temperatures.

A composite summary of all the data which were essential for the correlation is shown in Tables I to IV.

The data taken during the experimental runs were rather difficult to correlate for several reasons. In the first place, there had been no previous study of entrainment in an evaporator of this type to give any idea of the grouping of the variables in the equation. It was necessary to determine this entirely from the derivation given above. In this regard another handicap was the fact that one of the variables appearing in the derived equation, namely, the velocity of the curtain, could not be determined experimentally, making it necessary to use an unknown function of the other variables instead.

TABLE I

DATA AT 100° C. BOILING POINT

Series	Run	Abs. Pressure		Temperature		ΔT	Liquor Velocity	U	Density	
		Vapor mm.Hg.	Steam mm.Hg.	Vapor ° C.	Steam ° C.	° C.	ft./sec. u_L		Liquor Lb./cu. ft. ρ'	Vapor Lb./cu. ft. ρ
KL	1	743.1	889.3	99.37	104.46	5.09	6.05	561.0	63.83	0.03658
	2	743.1	888.5	99.37	104.40	5.03	5.9	556.0	63.83	0.03658
	3	743.2	886.3	99.38	104.36	4.98	7.7	632.2	63.83	0.03658
	4	743.2	888.8	99.38	104.41	5.03	7.6	622.7	63.83	0.03658
	5	743.2	889.8	99.38	104.47	5.09	11.1	644.0	63.83	0.03658
	6	743.2	890.2	99.38	104.49	5.11	11.1	661.5	63.83	0.03658
	7	743.2	889.2	99.38	104.46	5.08	13.0	688.4	63.83	0.03658
	8	743.2	889.2	99.38	104.46	5.08	13.0	699.7	63.83	0.03658
	9	743.2	889.4	99.38	104.46	5.08	15.7	825.0	63.83	0.03658
	10	743.2	889.2	99.38	104.46	5.08	15.7	813.9	63.83	0.03658
KM	1	732.1	1052.1	99.37	109.37	10.00	4.55	520.6	63.83	0.03658
	2	743.1	1052.1	99.37	109.37	10.00	4.55	503.1	63.83	0.03658
	3	743.1	1052.5	99.37	109.38	10.01	8.7	687.9	63.83	0.03658
	4	743.1	1052.2	99.37	109.38	10.01	8.7	670.7	63.83	0.03658
	5	742.5	1051.5	99.34	109.35	10.01	12.2	773.9	63.83	0.03651
	6	742.5	1053.1	99.35	109.40	10.05	12.2	748.4	63.83	0.03653
	7	742.5	1053.1	99.35	109.40	10.05	15.3	781.8	63.83	0.03653
	8	742.5	1054.2	99.35	109.43	10.08	15.3	790.7	63.83	0.03653
KN	1	742.5	1243.6	99.35	114.40	15.05	5.0	533.8	63.83	0.03653
	2	742.5	1243.1	99.35	114.39	15.04	5.0	538.0	63.83	0.03653
	3	742.5	1243.4	99.35	114.40	15.05	9.4	717.3	63.83	0.03653
	4	742.5	1242.9	99.35	114.39	15.04	9.3	677.2	63.83	0.03653
	5	740.8	1243.2	99.29	114.39	15.10	9.3	691.6	63.83	0.03644
	6	740.8	1241.0	99.29	114.34	15.05	12.3	769.3	63.83	0.03644
	7	740.8	1241.2	99.29	114.35	15.06	12.3	757.7	63.83	0.03644
	8	740.8	1240.8	99.29	114.34	15.05	14.9	820.0	63.83	0.03644
	9	740.8	1240.8	99.29	114.34	15.05	14.9	804.8	63.83	0.03644

TABLE II

DATA AT 70° C. BOILING POINT

Series	Run	Abs. Pressure		Temperature		ΔT	Liquor Velocity	U	Density	
		Vapor mm.Hg.	Steam mm.Hg.	Vapor ° C.	Steam ° C.	° C.	ft./sec. u_L		Liquor Lb./cu. ft. ρ'	Vapor Lb./cu. ft. ρ
KP	1	232.4	756.9	70.0	99.88	29.88	13.4	833.5	64.29	0.01236
	2	231.0	756.7	69.74	99.88	30.14	13.4	874.0	64.29	0.01222
	3	232.7	757.7	69.91	99.92	30.01	11.0	789.8	64.29	0.01230
	4	232.7	756.9	69.91	99.88	29.97	11.0	693.1	64.29	0.01230
	5	211.6	758.9	67.74	99.96	32.22	5.55	581.4	64.29	0.01127
	6	211.7	756.7	67.75	99.88	32.13	5.55	515.0	64.29	0.01127
	7	225.3	756.9	69.17	99.88	30.71	5.3	576.8	64.29	0.01194
	8	224.7	757.7	69.11	99.92	30.81	11.0	659.0	64.29	0.01191
KQ	1	228.1	525.0	69.45	89.96	20.51	13.5	764.9	64.29	0.01208
	2	228.1	523.1	69.45	89.86	20.41	13.4	769.6	64.29	0.01208
	3	228.1	522.8	69.45	89.85	20.40	10.3	697.7	64.29	0.01208
	4	228.1	523.4	69.45	89.88	20.43	10.3	673.5	64.29	0.01208
	5	232.0	522.4	69.84	89.83	19.99	7.5	635.2	64.29	0.01227
	6	232.1	521.5	69.85	89.78	19.93	7.5	639.2	64.29	0.01227
	7	230.1	521.4	69.65	89.78	20.13	5.0	517.6	64.29	0.01218
	8	230.1	522.3	69.65	89.82	20.17	5.0	513.7	64.29	0.01218
KR	1	229.9	349.7	69.63	79.62	9.99	5.0	557.5	64.29	0.01218
	2	229.0	350.7	69.54	79.69	10.15	5.0	553.9	64.29	0.01213
	3	230.0	352.2	69.64	79.79	10.15	5.0	488.3	64.29	0.01218
	4	229.1	350.5	69.55	79.67	10.12	8.2	667.9	64.29	0.01213
	5	230.1	349.5	69.65	79.60	9.95	8.2	673.5	64.29	0.01218
	6	230.1	350.1	69.65	79.64	9.99	10.8	712.0	64.29	0.01218
	7	230.1	349.3	69.65	79.59	9.94	10.7	727.8	64.29	0.01218
	8	230.1	351.9	69.65	79.78	10.13	14.0	749.2	64.29	0.01218
	9	230.1	350.1	69.65	79.64	9.99	14.0	729.8	64.29	0.01218

TABLE I

Data at 100° C. Boiling Point

Vapor Volume cu. ft./ sec.	Curtain Length in.	Curtain Area sq. ft.	Vapor Velocity ft./sec. u_v	Liquor Conc. %	Drips Conc. p.p.m.	E Lb. Liquor 10^6 x Lb. vapor	$\frac{E}{10^4\rho^{1.5}u_v}$	$\frac{E\rho'}{10^6\rho}$	$\frac{10^6\rho u_v^2}{\rho' u_L^{1.8}}$
0.5591	*	.....	.....	9.28	31.5	339.4	.....	.....	.....
0.5032	*	.....	.....	9.28	27.5	289.6	.....	.....	.....
0.5671	*	.....	.....	9.28	20.8	224.2	.....	.....	.....
0.6390	*	.....	.....	9.28	19.4	209.0	.....	.....	.....
0.6598	21	11.55	0.0571	9.28	6.7	72.19	17.83	0.1258	0.0245
0.7313	21	11.55	0.0633	9.28	4.9	52.80	11.8	0.0919	0.0302
0.7313	19	10.53	0.0694	9.28	3.87	41.71	8.45	0.0725	0.0275
0.7711	19	10.53	0.0732	9.28	3.34	35.99	6.94	0.0625	0.0305
0.8267	18	10.02	0.0825	9.28	2.93	31.57	5.38	0.0550	0.0251
0.8665	18	10.02	0.0865	9.28	2.83	30.49	4.97	0.0530	0.0275
1.318	*	.....	.....	9.28	4.84	52.6	.....	.....	.....
1.335	*	.....	.....	9.28	3.88	41.81	.....	.....	.....
1.972	14	8.02	0.246	9.28	10.03	108.1	6.21	0.188	0.538
1.915	14	8.02	0.239	9.28	10.05	108.2	6.37	0.188	0.532
2.168	14	8.02	0.270	9.28	12.10	130.4	6.94	0.227	0.465
2.176	14	8.02	0.271	9.28	14.39	155.1	8.10	0.270	0.466
2.325	15	8.51	0.273	9.28	17.6	189.7	9.96	0.330	0.315
2.325	15	8.51	0.273	9.28	18.4	198.3	10.4	0.345	0.315
2.412	13	12.59	0.192	9.28	9.7	104.5	7.83	0.182	1.157
2.332	23	12.59	0.185	9.28	9.3	100.2	7.93	0.175	1.085
3.200	21	11.55	0.277	9.28	14.0	150.9	7.80	0.262	0.778
3.336	21	11.55	0.289	9.28	11.6	125.0	6.19	0.218	0.861
3.279	21	11.55	0.284	9.28	10.6	114.2	5.78	0.200	0.833
3.744	19	10.53	0.355	9.28	9.0	96.99	3.93	0.170	0.788
3.528	19	10.53	0.335	9.28	8.2	88.37	3.81	0.154	0.701
3.750	17	9.51	0.394	9.28	8.18	88.14	3.21	0.154	0.688
3.846	17	9.51	0.404	9.28	8.0	86.20	3.07	0.150	0.723

* No curtain.

TABLE II

Data at 70° C. Boiling Point

Vapor Volume cu. ft./ sec.	Curtain Length in.	Curtain Area sq. ft.	Vapor Velocity ft./sec. u_v	Liquor Conc. %	Drips Conc. p.p.m.	E Lb. Liquor 10^6 x Lb. vapor	$\frac{E}{10^4\rho^{1.5}u_v}$	$\frac{E\rho'}{10^6\rho}$	$\frac{10^6\rho u_v^2}{\rho' u_L^{1.8}}$
19.46	9	5.64	3.451	7.67	171.0	2229	46.8	11.6	21.4
27.29	8	5.20	5.249	7.67	.....	.....	.....	.....	.....
27.71	10	6.10	4.544	7.67	97.0	1265	20.5	6.62	52.8
22.21	10	6.10	3.642	7.67	97.0	1265	25.5	6.62	33.8
22.99	11	6.57	3.501	7.67	74.05	965.4	23.1	5.52	97.8
21.24	11	6.57	3.234	7.67	62.9	820.4	21.3	4.69	83.4
20.49	11	6.57	3.123	7.67	87.2	1137	27.9	6.13	89.9
27.05	9	5.64	4.796	7.67	44.7	582.8	9.35	3.14	56.8
17.75	12	7.04	2.521	7.67	76.1	992.2	28.7	5.28	11.0
15.91	12	7.04	2.311	7.67	78.1	1018	33.1	5.41	9.36
15.45	13	7.53	2.053	7.67	24.8	323.3	11.8	1.72	11.85
14.92	13	7.53	1.983	7.67	20.8	271.4	10.3	1.44	11.1
10.07	14	8.02	1.255	7.67	24.9	324.6	19.0	1.72	9.15
10.73	14	8.02	1.338	7.67	21.3	277.7	15.3	1.48	10.45
11.27	16	9.02	1.249	7.67	20.6	268.6	15.9	1.43	16.3
10.15	16	9.02	1.126	7.67	20.8	271.2	17.9	1.44	13.22
7.149	*	.....	.....	7.67	9.1	118.7	.....	.....	.....
5.419	*	.....	.....	7.67	8.7	113.4	.....	.....	.....
4.871	*	.....	.....	7.67	6.93	90.35	.....	.....	.....
6.337	18	10.02	0.6323	7.67	3.4	44.33	5.11	0.234	1.71
6.645	18	10.02	0.6330	7.67	4.45	58.02	6.52	0.306	1.89
6.933	15	8.51	0.8141	7.67	8.1	105.6	9.66	0.556	1.73
7.069	15	8.51	0.8303	7.67	7.9	103.0	9.22	0.544	1.82
7.509	12	7.04	1.066	7.67	8.3	108.2	7.53	0.571	1.86
7.461	12	7.04	1.059	7.67	6.3	82.13	5.78	0.434	1.83

* No curtain.

TABLE III

DATA AT 80° C. BOILING POINT

Series	Run	Abs. Pressure		Temperature		ΔT	Liquor Velocity	U	Density	
		Vapor mm.Hg.	Steam mm.Hg.	Vapor ° C.	Steam ° C.	° C.	ft./sec. u_L		Liquor Lb./ cu. ft. ρ'	Vapor Lb./ cu. ft. ρ
KS	1	349.5	520.8	79.60	89.75	10.15	14.7	785.7	63.72	0.01801
	2	349.2	521.0	79.58	89.76	10.18	14.7	812.3	63.72	0.01801
	3	349.2	521.0	79.58	89.77	10.19	10.4	731.0	63.72	0.01801
	4	349.2	521.2	79.58	89.77	10.19	10.4	772.0	63.72	0.01801
	5	347.6	519.6	79.47	89.69	10.22	7.6	641.5	63.72	0.01792
	6	347.6	519.6	79.47	89.69	10.22	7.6	635.3	63.72	0.01813
	7	346.5	518.5	79.40	89.63	10.23	4.7	535.8	63.72	0.01788
	8	346.5	518.5	79.40	89.63	10.23	4.7	547.4	63.72	0.01788
KT	1	350.2	720.0	79.65	98.49	18.84	4.4	571.6	63.72	0.01805
	2	350.2	720.6	79.65	98.51	18.86	4.4	564.8	63.72	0.01805
	3	350.2	720.4	79.65	98.50	18.85	7.9	761.0	63.72	0.01805
	4	350.2	720.2	79.65	98.50	18.85	7.9	742.3	63.72	0.01805
	5	348.7	718.1	79.55	98.42	18.87	10.8	832.8	63.72	0.01799
	6	348.7	718.6	79.55	98.44	18.89	10.8	815.6	63.72	0.01799
	7	348.7	718.5	79.55	98.43	18.88	14.0	887.4	63.72	0.01799
	8	348.7	718.7	79.55	98.45	18.90	14.0	871.2	63.72	0.01799
KU	1	347.5	628.5	79.48	94.76	15.28	13.6	815.6	63.72	0.01794
	2	347.5	628.5	79.48	94.76	15.28	13.6	796.8	63.72	0.01794
	3	347.6	628.6	79.48	94.76	15.28	10.9	766.4	63.72	0.01794
	4	347.6	629.6	79.48	94.81	15.33	10.9	775.4	63.72	0.01794
	5	347.2	628.2	79.44	94.75	15.31	7.9	671.1	63.72	0.01791
	6	347.2	628.2	79.44	94.75	15.31	7.9	667.0	63.72	0.01791
	7	347.2	628.5	79.44	94.76	15.32	4.2	478.1	63.72	0.01791
	8	347.2	628.2	79.44	94.75	15.31	4.2	482.8	63.72	0.01791

* No reading.

TABLE IV

DATA AT 90° C. BOILING POINT

Series	Run	Abs. Pressure		Temperature		ΔT	Liquor Velocity	U	Density	
		Vapor mm.Hg.	Steam mm.Hg.	Vapor ° C.	Steam ° C.	° C.	ft./sec. u_L		Liquor Lb./ cu. ft. ρ'	Vapor Lb./ cu. ft. ρ
KV	1	522.1	1072.2	89.81	109.94	20.13	4.5	559.8	63.08	0.02624
	2	523.2	1071.0	89.87	109.90	20.03	4.5	568.3	63.08	0.02629
	3	520.6	1069.1	89.74	109.85	20.11	8.0	718.6	63.08	0.02617
	4	521.4	1073.2	89.78	109.96	20.18	8.1	704.6	63.08	0.02621
	5	523.6	1073.0	89.89	109.96	20.07	10.8	796.2	63.08	0.02632
	6	521.6	1072.8	89.79	109.95	20.16	10.8	784.1	63.08	0.02620
	7	523.8	1066.8	89.90	109.78	19.88	13.4	860.6	63.08	0.02634
	8	524.2	1066.3	89.92	109.77	19.85	13.4	938.7	63.08	0.02635
KW	1	522.6	907.6	89.84	105.05	15.21	14.1	807.6	63.08	0.02627
	2	519.1	906.4	89.66	105.01	15.35	14.1	796.6	63.08	0.02611
	3	521.3	906.6	89.77	105.02	15.25	10.5	756.5	63.08	0.02620
	4	521.8	906.9	89.80	105.03	15.23	10.5	776.6	63.08	0.02625
	5	520.7	904.8	89.74	104.96	15.22	8.1	721.4	63.08	0.02617
	6	520.7	904.5	89.74	104.95	15.21	8.1	721.9	63.08	0.02617
	7	520.7	904.9	89.74	104.97	15.23	5.1	600.6	63.08	0.02617
	8	520.7	904.7	89.74	104.96	15.22	5.1	597.0	63.08	0.02617
KX	1	518.5	756.8	89.63	99.88	10.25	5.4	657.5	63.08	0.02607
	2	518.0	757.9	89.60	99.93	10.33	5.4	635.9	63.08	0.02604
	3	518.5	758.5	89.63	99.94	10.31	7.8	714.7	63.08	0.02607
	4	518 5	759.4	89.63	99.98	10.35	7.8	700.8	63.08	0.02607
	5	518.1	758.9	89.60	99.96	10.36	11.0	821.3	63.08	0.02604
	6	518.5	759.5	89.63	99.98	10.35	11.0	805.0	63.08	0.02607
	7	518.5	758.1	89.63	99.93	10.30	14.4	854.5	63.08	0.02607
	8	518.5	757.5	89.63	99.91	10.28	14.4	833.5	63.08	0.02607

TABLE III

Data at 80° C. Boiling Point

Vapor Volume cu. ft./ sec.	Curtain Length in.	Curtain Area sq. ft.	Vapor Velocity ft./sec. u_v	Liquor Conc. %	Drips Conc. p.p.m.	E Lb. Liquor 10^6 x Lb. vapor	$\frac{E}{10^4\rho^{1.5}u_v}$	$\frac{E\rho'}{10^6\rho}$	$\frac{10^6\rho u_v^2}{\rho' u_L^{1.8}}$
4.287	12	7.04	0.6085	7.18	6.9	96.10	6.54	0.341	0.827
5.241	12	7.04	0.7440	7.18	7.0	97.5	5.43	0.345	1.24
5.063	13	7.53	0.6725	7.18	*	.....	.....	.....	.....
4.949	13	7.53	0.6573	7.18	*	.....	.....	.....	.....
4.204	13	7.53	0.5584	7.18	*	.....	.....	.....	.....
4.135	13	7.53	0.5492	7.18	*	.....	.....	.....	.....
3.365	*	.....	.....	7.18	*	.....	.....	.....	.....
3.495	*	.....	.....	7.18	*	.....	.....	.....	.....
7.326	16	9.02	0.8127	7.18	23.1	321.8	16.4	1.14	12.95
7.280	16	9.02	0.8074	7.18	22.8	317.6	16.3	1.12	12.8
9.563	14	8.02	1.192	7.18	18.6	259.0	8.98	0.915	9.74
9.658	14	8.02	1.204	7.18	18.8	261.8	8.98	0.924	9.92
11.00	14	8.02	1.371	7.18	21.7	302.2	9.14	1.07	7.34
10.67	14	8.02	1.330	7.18	20.6	286.9	8.96	1.012	6.90
11.74	16	9.02	1.303	7.18	13.2	183.9	5.84	0.649	4.16
11.28	16	9.02	1.251	7.18	13.3	185.2	6.13	0.655	3.82
8.584	17	9.51	0.9022	7.18	9.4	130.9	6.04	0.464	2.06
8.290	17	9.51	0.8714	7.18	8.94	124.5	5.81	0.442	1.93
7.787	18	10.02	0.7769	7.18	7.8	108.6	5.81	0.386	2.30
8.177	18	10.02	0.8158	7.18	9.9	137.9	7.02	0.489	2.54
4.498	13	7.53	0.5974	7.18	11.5	160.2	11.1	0.570	2.42
6.916	13	7.53	0.9187	7.18	11.1	154.6	7.04	0.548	5.58
4 699	20	11.04	0.4255	7.18	9.0	125.3	12.3	0.441	3.86
4.699	20	11.04	0.4255	7.18	10.9	151.8	14.8	0.539	3.86

TABLE IV

Data at 90° C. Boiling Point

Vapor Volume cu. ft./ sec.	Curtain Length in.	Curtain Area sq. ft.	Vapor Velocity ft./sec. u_v	Liquor Conc. %	Drips Conc. p.p.m.	E Lb. Liquor 10^6 x Lb. vapor	$\frac{E}{10^4\rho^{1.5}u_v}$	$\frac{E\rho'}{10^6\rho}$	$\frac{10^6\rho u_v^2}{\rho' u_L^{1.8}}$
4.122	12	7.04	0.5852	6.65	44.9	675.1	27.2	1.62	9.48
3.626	12	7.04	0.5148	6.65	41.6	625.6	28.6	1.151	7.22
6.615	13	7.53	0.8806	6.65	7.5	112.8	3.02	0.272	7.55
6.412	13	7.53	0.8515	6.65	8.45	126.8	3.51	0.305	6.97
6.658	12	7.04	0.9452	6.65	36.6	550.4	13.6	1.32	5.12
6.688	12	7.04	0.9495	6.65	33.8	508.3	12.6	1.22	5.18
8.865	10	6.10	1.454	6.65	22.6	339.8	5.46	0.818	8.30
7.691	10	6.10	1.261	6.65	27.2	409.1	7.59	0.987	6.18
5.405	12	7.04	0.7674	6.65	5.7	85.72	2.62	0.202	2.10
5.527	12	7.04	0.7848	6.65	5.9	88.72	2.67	0.211	2.18
5.869	14	8.02	0.7318	6.65	6.8	102.3	3.29	0.246	3.23
5.042	14	8.02	0.6287	6.65	6.4	96.25	3.59	0.228	2.34
3.572	16	9.02	0.3962	6.65	20.0	300.7	17.9	0.724	1.50
3.921	16	9.02	0.4349	6.65	20.0	300.7	16.3	0.724	1.82
3.761	18	10.02	0.3753	6.65	26.3	395.5	24.9	0.951	3.10
3.560	18	10.02	0.3552	6.65	26.1	392.4	26.0	0.945	2.79
1.372	17	9.51	0.1442	6.65	12.6	189.5	31.3	0.460	0.415
1.385	17	9.51	0.1455	6.65	11.6	174.4	28.6	0.424	0.420
1.673	14	8.02	0.2085	6.65	7.8	117.3	13.4	0.285	0.444
1.851	14	8.02	0.2309	6.65	7.5	112.8	11.6	0.274	0.543
3.682	12	7.04	0.5225	6.65	5.95	89.48	4.07	0.218	1.50
3.509	12	7.04	0.4980	6.65	6.24	93.85	4.47	0.228	1.36
3.811	11	6.57	0.5803	6.65	9.83	147.8	6.04	0.359	1.05
3.669	11	6.57	0.5589	6.65	10.4	156.4	6.64	0.380	0.988

Since the vapor velocity under any given operating conditions could not be predicted, no series of runs could be made at constant vapor velocity in order to determine the exact nature of this function.

As was stated above the value of C, although a function of the velocity with which the liquid leaves the tubes, could not be determined experimentally. The material coming from the tubes is a

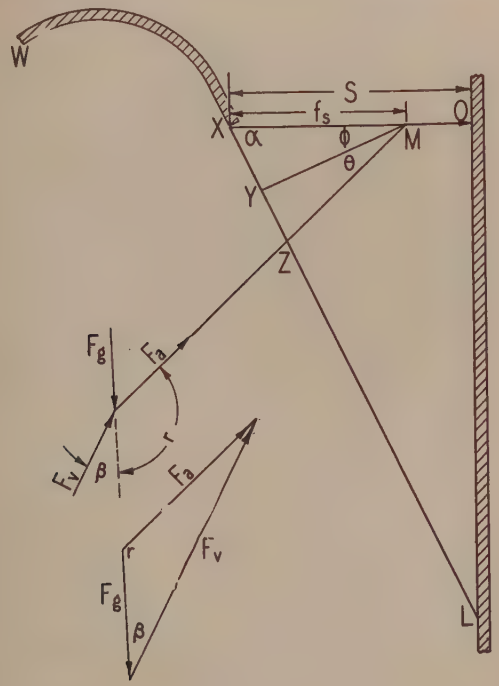

Fig. 4. Diagram of Forces Acting on the Curtain.

mixture of liquid and vapor so that its velocity is probably a function of the volume of the liquid or vapor, or both. Since the relation between the two is unknown it was necessary to ascertain which one, used alone, gave the better correlation.

Examination of the derivation indicates that the exponent of u_v and C should be approximately the same. The ratios $\frac{u_v}{V_v}$ and $\frac{u_v}{u_L}$

were plotted against E at constant vapor density. The points $\frac{u_v}{V_v}$ vs. E were widely scattered and did not show any relationship; however, those of $\frac{u_v}{u_L}$ were quite closely grouped. In comparison with the previous plot of u_v vs. E the introduction of the factor $\frac{1}{V_v}$ destroyed the correlation while $\frac{1}{u_L}$ drew the points together. This would indicate that u_v should be divided by some variable such as C, and that since C is unknown u_L is the most suitable known variable to be used in its place.

Accordingly, if C^m is replaced by ${u_L}^{m'}$ and the constant N is combined in the main constant the equation will be

$$E = \left(\frac{\rho}{\rho'}\right)^{\delta-1} \cdot \lambda' \left(\frac{\rho {u_v}^2}{\rho' {u_L}^{m'}}\right)$$

The general form of the equation evidently coincides with the derived equation but it is necessary to evaluate the exponents. For the first approximation m′ was assumed to be 2 and ρ' was omitted because it was essentially constant throughout. $\frac{\rho {u_v}^2}{{u_L}^2}$ when plotted against E formed bands of constant vapor density which, although they overlapped somewhat due to rather scattered data, were quite distinct and of the same slope. By trial and error it was found that the bands would coincide if each set of values was multiplied by the corresponding vapor density; thereby indicating that $\delta - 1 = 1$ or $\delta = 2$. The band composed of all the points is somewhat curved but to simplify the next step in the correlation, it could be fairly well represented by a line having a slope of ½, so that an approximate expression would be

$$E = K\rho \left(\frac{\rho {u_v}^2}{\rho' {u_L}^{m'}}\right)^{1/2}$$

then

$$\frac{E}{\rho^{1.5} u_v} = K \left(\frac{1}{{u_L}^{\frac{2'm'}{4}}}\right)^{1/2}$$

When $\frac{E}{\rho^{1.5} u_v}$ is plotted against u_L^2 the most reliable points form a band with a slope determined to be —0.45.

If $\frac{m'}{4} = 0.45$; m′ is 1.8 and can be substituted in the original expression.

$$E = \frac{\rho}{\rho'} \cdot \lambda' \left(\frac{\rho u_v^2}{\rho' u_L^{1.8}} \right)$$

or

$$\frac{E\rho'}{\rho} = \lambda' \left(\frac{\rho u_v^2}{\rho' u_L^{1.8}} \right)$$

The density of the liquid, ρ′, is again included in the equation purely on the basis of the derivation and dimensional analysis. Since it did not vary appreciably at any time, there is no experimental proof that it should be a factor.

Although various methods were used to determine the nature of the λ′ function, it did not resolve itself into any of the simpler relationships and for this reason it was considered more desirable to leave the equation in the above form and express the function as a plot.

The plot of

$$\frac{\rho u_v^2}{\rho' u_L^{1.8}} \text{ vs. } \frac{E\rho'}{\rho} \text{ which equals } \lambda' \left(\frac{\rho u_v^2}{\rho' u_L^{1.8}} \right)$$

is shown in Figure 5. The points fall into a band, which may include a series of parallel lines due to the influence of another factor that is not present in the equation. It is possible that this variable is the structure of the curtain. One of the assumptions made in the derivation of the equation was that the curtain should be uniform and free from holes or raggedness. It would perhaps be possible to obtain such a condition in an evaporator with several rows of fairly large tubes where the large amount of liquor circulated would produce a heavy curtain. In the evaporator used for this study, however, the heating element contained only a single row of ½ inch tubes giving a very light curtain, easily affected by slight fluctuations; so that the entrainment varied irregularly as the structure of the curtain changed. Although the variation in this case was, therefore, quite large due to the lightness of the curtain and a heavier curtain would undoubtedly narrow the band, the existence and magnitude of such a variable can-

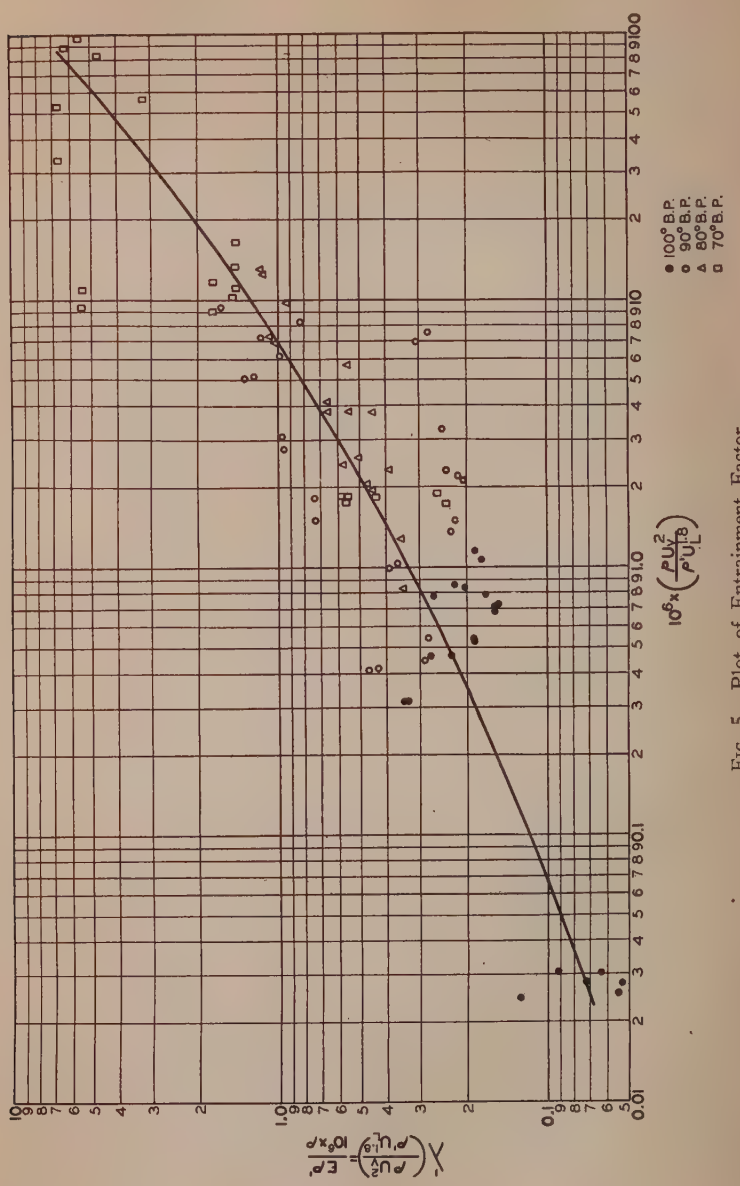

FIG. 5. Plot of Entrainment Factor.

not be proven because the only experimental means of detecting any difference in the curtain is by qualitative observation.

In those runs where the volume of vapor passing out of the tubes was comparatively large the whole edge of curtain was blown upward by the force of the vapor. This occurs whenever the vapor velocity passes a certain critical value, definite for each evaporator. The amount of entrainment under these circumstances is very great, and does not follow the same relationship that it does when the vapor velocity is below the critical. Accordingly, the points on the plot corresponding to these runs are much higher than the average and are considerably out of line.

There are some indications that the amount of liquid in the curtain has an influence. The points of a few of the series lie in the same relative order as the liquor velocities; but in the majority of cases other indeterminate ractors evidently enter and alter the relationship so that no conclusions can be drawn in this regard. A single line has, therefore, been drawn through the points to give an average value for the entrainment factor.

Conclusion

As a result of this research, it can be concluded that the amount of entrainment in a forced circulation evaporator when using a non-foaming liquid is given by the equation

$$E = \frac{\rho}{\rho'} \cdot \lambda' \left(\frac{\rho u_v^2}{\rho' u_L^{1.8}} \right)$$

The λ' function will, in general, follow the form of the plot shown in Figure 5. The actual values given for the function, however, apply only for a liquid with a surface tension and viscosity essentially the same as those of water and for an evaporator whose dimensions in the vicinity of the deflector have the same relation as those of the evaporator used in this study and shown in Figure 3.

Acknowledgment

Appreciation is expressed to Mr. W. R. Kleckner and Mr. L. A. Logan for their assistance in obtaining the experimental data, and to the Board of the Graduate School of the University of Michigan for their assistance in making possible the completion of this research.

Nomenclature

E Entrainment, lbs. liquor per million lbs. vapor.
ρ Density of vapor, lbs. per cu. ft.
ρ' Density of liquor, lbs. per cu. ft.
D Diameter of largest droplets.
F_g Force exerted by gravity.
F_v Force exerted by vapor.
F_a Accelerating force.
u_v Velocity of vapor through curtain, ft. per sec.
u_L Velocity of liquor through tubes, ft. per sec.
C Velocity of liquor leaving deflector, ft. per sec.
f Fraction defined in assumption 3.
s Distance from deflector tip to wall.
α Angle deflector makes with horizontal.
β Angle vapor makes with vertical (assumption 2).
γ Angle accelerating force makes with vertical.
v_L Volume of liquor carried per million cu. ft. vapor.
v_v Volume of vapor leaving tubes, cu. ft. per sec.
g Acceleration of gravity.
$\left(\frac{D'u\rho}{z}\right)$ Reynold's Criterion for the vapor.
A, B, k, N, m, b, ψ, δ, constants.

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3. Hausbrand, Evaporating, Condensing, and Cooling Apparatus, Revised, D. Van Nostrand Co., 1929.
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Discussion

(Summarized by T. H. Chilton, Chairman of the Sub-Committee on Papers)

H. W. Mahr inquired about the effect of viscosity on entrainment. W. L. Badger replied that no data were at present available, the experimental work having been confined to solutions not more than 10% in NaCl. T. H. Chilton remarked that surface tension might be an important factor, particularly the kinetic surface tension as suggested in the papers on foaming of boilers. W. L. Badger stated that he had discussed this subject with Prof. Foulk and the latter did not believe his methods were applicable since a mixture of vapor and liquid is formed in the forced circulation evaporator and later separated. M. J. Kermer pointed out that it is possible, even in a natural circulation evaporator, to get excessive entrainment and stated it is his opinion that the curtain formed by the deflector might not be the ideal way to remove the entrained liquor since the vapor must pass through the curtain. W. L. Badger replied that the curtain consists of successive drops of liquid and is not actually continuous. The pressure drop through the curtain is, therefore, too small to measure. Under ordinary circumstances the vapor in a forced circulation evaporator is remarkably free from entrainment, although if the steam velocity is too high the curtain will turn up and excessive entrainment will result. T. H. Chilton expressed the hope that data on this critical velocity through the curtain would be obtained in subsequent work. In written discussion T. H. Chilton reports that the data on entrainment in this paper can be approximated by calculation:

$$E = 1200\, G^{1.5}$$

where E = pounds of liquor per million pounds of vapor and
G = mass velocity of the vapor passing the deflector in a horizontal plane in pounds per sq. ft. per sec.

O. C. Cessna (written) replied that the liquor velocity should, in his opinion, be included and the grouping suggested in the paper appears to be the best that will bring in this factor, although the above correlation (by Chilton) is probably as good for practical purposes.

SOME CHEMICAL ASPECTS OF COAL UTILIZATION

By H. H. LOWRY *

The very considerable increase in the efficiency of utilization of coal by industry within the past two decades may be attributed primarily to advance in methods of handling materials and controlling operations, to the improvement of auxiliary equipment—such as the steam turbine in power generation—and to the development of materials capable of withstanding higher temperatures and pressures. During this period of rapid growth in the engineering aspects of coal utilization, knowledge has been accumulating steadily regarding the chemical nature of coal. It must be recognized that in order to yield the desired result in any field of utilization, coal must undergo a series of chemical reactions, and that, therefore, the chemical aspects of the use of coal as a raw material must continue to assume increasing importance as the mechanical equipment associated with its use approaches perfection. To get the most from coal, as well as the most for coal, the coal technologist and the coal producer must have a more thorough understanding of the chemical reactions involved in combustion, coking, gasification, and hydrogenation processes and as complete a knowledge as possible of the chemical nature of the coal used. Much fundamental scientific study needs to be given to each of these complex chemical processes.

The Chemical Nature of Coal [1]

Coal is of vegetable origin and is derived from cellulose and/or lignin and other plant constituents. During geologic ages, the original deposit has been subjected to pressures and temperatures of different intensities. Various stages in the coalification process may be recognized in coals available for use. Analyses of coals, from peat through lignite, bituminous coal, anthracite to graphite show no sharp demarcation between ranks. On the other hand, if the results of analyses of coals for carbon, hydrogen and oxygen, on an ash and

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moisture free basis, are plotted on triangular coordinates, as in Fig. 1, a continuous "coal band" is obtained which includes a great majority of published analytical data.[2] That the coal band lies between a line starting at water, passing through cellulose, and ending at carbon—a line of dehydration—and another line starting at CO_2, similarly passing through cellulose, and ending on the line of zero oxygen—

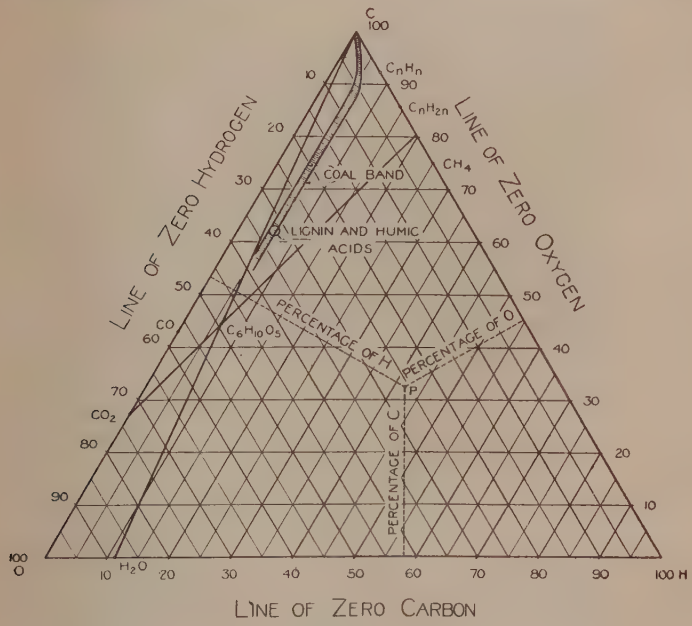

FIG. 1. The "Coal Band" Plotted on Triangular Co-ordinates for % C + % H + % O = 100.

a line of decarboxylation—shows graphically that the initial stages of coalification result primarily from dehydration and decarboxylation of the original vegetable matter. The change in direction of the coal band for the higher rank coals may be explained similarly, by loss of methane due to higher effective temperatures. These considerations suggest that there may be expected to be in coal the more stable nuclei of the original organic matter condensed and polymerized to highly complex structures. Although the analytical data emphasize that every coal must be considered as an individual, investiga-

tions of the chemical nature of coal indicate that these stable nuclei are very similar in coals of different ranks and from different localities.

Peat is in part soluble in alkali. The soluble products are classed as humic acids. As the metamorphosis of coals proceeds, the proportion of alkali soluble humic acids decreases to zero in a true bituminous coal. However, it is important to note that so-called "humic acids" may be regenerated by mild oxidation from high rank bituminous coals in amounts as great as 85% of the coal substance. These facts

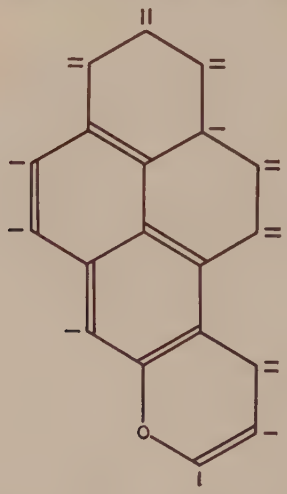

FIG. 2. The Nucleus of "Humic Acids" according to Fuchs [3]: an Important Structural Unit of Coal.

support the hypothesis of the persistence of stable nuclei through the stages of coalification. Our knowledge of the chemical structure of these nuclei is very limited and is based largely on incomplete information regarding the structure of the humic acids themselves. The work of Fuchs [3] and others definitely indicates that the nuclei of humic acids are polycyclic and contain six-carbon rings. (Fig. 2.) It is suggested that these nuclei may condense by elimination of active side groups by interaction with similar units or by reaction with other constituents present in the original vegetable matter. Further study of the chemical structure of humic acids should throw much additional light on the more complex chemical structure of coal.

Many studies have been made of the reaction of simple chemical reagents on coal. The work of Bone and collaborators [4] on the oxidation of coal with alkaline permanganate at 100° C. has shown that the six-carbon nucleus is an essential unit of structure confirming, in this respect, earlier work on oxidation under milder conditions. Besides CO_2, yields of 49% benzene carboxylic acids were obtained together with smaller amounts of oxalic and succinic acids as shown in Table I. Because of its well known stability and its presence in coal, it is not surprising that six-carbon ring compounds are found in the products from every known treatment of coal, including reaction with other reagents, such as the halogens and reducing agents, and thermal decomposition.

Coal is an extremely cheap chemical raw material and therefore a study of the reactions of coal and simple reagents may possibly prove of interest to both the coal and the chemical industries. The work of Bone just cited suggests that coal may well prove to be a source of simpler organic acids. The more complex humic acids may also have future commercial interest. The change in the slip characteristics of clay produced by the addition of humic acids has been utilized in the ceramic industry since biblical times. This same property may be utilized in soil conditioning. Furthermore, due to their acidic properties, humic acids from coal may be used to fix ammonia for fertilizer in a similar manner to that now being studied for peat by the Bureau of Chemistry and Soils.[5] A more complete understanding of the mechanism of oxidation of coals should also be of value in indicating possible chemical means of preventing deterioration on storage of coal, by use of oxidation inhibitors as has proven so successful in the rubber industry.

TABLE I

CARBON BALANCE OF THE OXIDATION OF COAL [4]

Original Carbon of the Coal Substance Appearing as	"Morwell" %	"Busty" %
Carbonic Anhydride	41.3	42.4
Acetic Acid	2.5	1.7
Oxalic Acid	7.7	6.5
Succinic Acid	0.8	nil
Benzenoid Acids	47.4	48.8
Total Carbon Accounted for	99.7	99.4

The oxidation products of coal may not be the only ones of possible interest to the chemical industry.

Considering the importance of the six-carbon ring in the chemical structure of coal, it is not surprising that hexachlorbenzene is to be found in the products of the reaction of coal and chlorine.[6] Further study of this reaction may indicate that coal should be considered as a raw material for the production of chlorinated organic compounds having value in the solvent industry or compounds similar in properties to the Halowaxes and Arochlors now on the market. Many of the other reactions of coal deserve more careful consideration than they have received so far.

Hydrogenation

Much work has been done on the preparation of a petroleum substitute by reaction of coal with hydrogen at high temperatures and pressures in the presence of catalysts. Recent reports of the decision of the Imperial Chemical Industries to erect a plant to hydrogenate 400 tons of coal per day, with a Government subsidy in the form of a tax on imported gasoline and light oils, indicate that progress has been made towards the development of an economic process. Hydrogenation may well serve as an example of where the engineer has advanced in the chemical processing of coal with a very incomplete knowledge of the chemical nature and reactions of the coal itself. In the hydrogenation process, the coal is suspended in a liquid medium which exerts an unknown solvent, or dispersing, action on the coal; the mixture is then treated with hydrogen, which reacts in an unknown way, at an elevated temperature which itself has an unknown effect on the coal used. From the strictly chemical point of view, the present progress has been made by excellent and systematic but empirical variation of the above mentioned factors, together with a study of the effects of different catalysts, etc. This procedure is a necessary consequence of our present lack of knowledge of the chemical, coal.

A real understanding of the chemistry of the hydrogenation of coal awaits further work on the chemical nature of the coal used and of the chemical compounds produced in the reaction. With exception of the work of Heyn and Dunkel, Ormandy and Craven, Pertierra, and Varga and von Makray,[7] no report appears to have been published on the isolation of individual chemical compounds produced in the hydrogenation of coal. General classification of the nature of the products has been based largely on solubility in certain solvents.

However, among the reaction products, benzene, toluene, and xylene and their hexahydroderivatives, naphthalene and its tetra- and decahydroderivatives, phananthrene and certain paraffins and hydroaromatics have been isolated, in addition to aromatic bases, phenol and higher phenols. The large number of six-carbon ring compounds may be noted as further confirmation of the importance of this unit structure in coal itself.

In connection with the preparation of petroleum substitutes from coal, the work of Berl and collaborators [8] on the preparation of artificial "coal" and "petroleum" from cellulose and lignin by heating in aqueous media under pressure appears of interest. In this work it was shown that the products obtained from cellulose in the weaker alkali solutions resembled coal, while those obtained in the stronger alkali solutions resembled petroleum. For cellulose or coal, both of which contain oxygen, decarboxylation would be favored by increasing the alkali concentration while dehydration would be retarded by the presence of water. With no dehydration and complete decarboxylation, the end product obtained from cellulose would consist of only carbon and hydrogen combined in the ratio shown in Figure 1 where the line of decarboxylation cuts the C-H axis. From this same point of view, the work of Fry [9] on the elimination of oxygen-containing groups from pure organic compounds by treatment with fused alkali is of considerable interest.

Coking and the Thermal Decomposition of Coal

In the above reactions as in every field of utilization of coal, it is necessary to apply heat to the coal. With our lack of knowledge of the chemical constitution of coal, the nature of the pyrolytic reactions is necessarily still unknown. The numerous investigations of the coking and caking characteristics of coals and of methods for evaluating them for by-product coking have indicated in a general way the nature of the coking process and at the same time clearly show the incompleteness of our knowledge of the quantitative chemical aspects of the thermal decomposition of coal.

Disregarding other coking processes, it is possible to present a generalized picture of by-product coal carbonization. A raw coal of unknown chemical constitution is charged into an oven whose walls are heated to some fixed high temperature. The coal immediately in contact with the walls is heated extremely rapidly to the maximum

temperature of the oven while the coal at the center of the charge is heated at a rate determined by the thermal conductivity of the mass and the temperature gradient, neither of which are generally known. The intervening coal layers are heated at intermediate rates. Surprising as it may at first appear, no thorough investigation has yet been reported on the separate effects of the rate of carbonization and the maximum temperature of carbonization, due in part to experimental difficulties involved. This is one of the studies being undertaken by the Coal Research Laboratory.

During the heating period, the coal passes through several poorly defined stages. The first effects of heat are commonly supposed to be the elimination of free water, and water and carbon dioxide by decomposition of the more unstable groups of the coal itself. As the temperature is raised, the coal softens, or melts, into what is frequently assumed to be, and called, a plastic state. It has been suggested that [10] this plastic condition results from melting of constituents of the original coal, or of "primary" decomposition products, below their decomposition temperatures, and subsequent solution or dispersion of the solid residue. During the plastic stage, there is a more or less marked swelling of the coal accompanied by active evolution of the volatile condensable components recovered in the tar, together with gases rich in hydrocarbons. As the temperature of the mass increases, the decomposition products become less and less rich in a condensable fraction and more and more rich in gases. The end of the carbonization period in high temperature coking is marked by a shrinking of the residue, coke, and by an increasing ratio of hydrogen to methane in the gas evolved. The hydrogen in the gas is commonly attributed to cracking of hydrocarbon gases. That this assumption may not be entirely correct is indicated by studies of the gases evolved on heating carbonaceous residues prepared at temperatures below the maximum temperatures, 950-1100°C, normally employed in the carbonization industry,[11] and by considerations discussed in the following paragraphs.

The plastic stage in the carbonization process is well recognized as being of the greatest importance in determining the character of the coke obtained. Many tests have been developed to evaluate coking coals by empirical methods designed to subject the coal to conditions qualitatively, but not quantitatively, similar to those existing in commercial coke ovens. Chemically, the quantitative conditions of rate of heating and rate of removal of the volatile components may

be of greatest importance. Without attempting, for the moment, to distinguish between the melting, or solvent action, of components originally present in the coal and the melting, or solvent action, of the primary products of thermal decomposition, it may be demonstrated that both the rate of heating and rate of removal of the volatile components may have a profound effect on the plastic stage. At any temperature, a chemical compound in a mixture will have a definite rate of evaporation depending on its partial pressure, a definite rate of thermal decomposition depending on its thermal stability, and a definite rate of solvent or dispersion action depending on the physical state of the mixture. It is evident that all these rates will not be the same function of temperature. If the external pressure is maintained so low that each decomposition product will evaporate or sublime as rapidly as formed, a normal coking coal may be heated to high temperatures without passing through a plastic stage as shown by the work of Juettner and Howard [12] in a study of the distillation of coal at a millionth of an atmosphere. The yield of volatile matter, in a given temperature range, likewise depends on the rate of heating and on the solvent action of the molten constituents of the coal. If the temperature is increased rapidly, the rate of distillation may become so great that insufficient time is given to thermally unstable compounds to decompose. This is illustrated by Figure 3, taken from the work of Juettner and Howard, where "curve (1)" represents the yields of condensable material obtained in a high vacuum stepwise distillation of a high volatile Pittsburgh coal extending over a period of 108 hours to the maximum temperature, and where "curve (2)" represents the yields obtained by heating in one hour to the temperature indicated by the crosses. In this case, not only was the yield of volatile condensable material almost doubled by the more rapid heating, but the character of the residue was very different; with the increased rate of heating, the primary products of decomposition were not removed by evaporation and sublimation as rapidly as they were formed, at temperatures above about 400°C, and the character of the residue indicated that they were in a molten condition sufficiently long to exert some solvent action on the residue and transform it to an apparently well fused mass. That this solvent action may, in part, account for the increased yield is indicated by consideration of "curve (3)," Figure 3, which represents the yield of condensable products obtained in an atmospheric distillation of the same coal under approximately the same condition of rate of

heating as for "curve (2)." The rate of evaporation of the products of decomposition in an atmospheric distillation is much less than in a high vacuum distillation and consequently a longer time is permitted for the initial decomposition products to dissolve the coal residue.

That solvent action may, in itself, be regarded as an extremely mild type of thermal decomposition and not necessarily only an extraction, or solution process, of substances having prior existence as such, follows from several elementary considerations. Electrostatics states

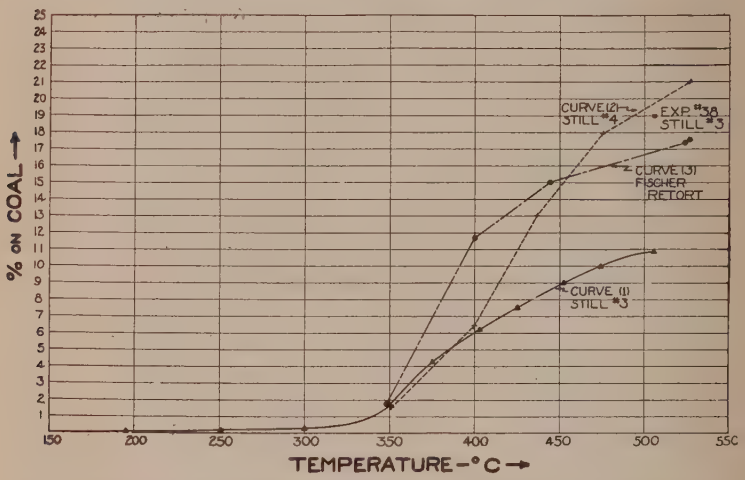

FIG. 3. Yields of Condensate as a Function of Temperature of Distillation for Edenborn Coal.[12]

Curve (1): High Vacuum Distillation—stepwise, cumulative.
Curve (2): High Vacuum Distillation—single stage, non-cumulative.
Curve (3): Distillation at Atmospheric Pressure under Conditions Similar to (2).

that the force holding oppositely charged bodies is less, the higher the dielectric constant of the medium in which the bodies exist. The forces holding atoms together in molecules and molecules together in a solid such as coal may be regarded as electrostatic in nature, and differ not in kind but in intensity. Coal normally may be regarded as existing in a medium, air, of dielectric constant unity; when impregnated with a solvent such as benzene, pyridine, or its own decomposition products, it exists in a medium of higher dielectric constant, and,

therefore, less energy in the form of heat is required to effect rupture of bonds. Once the bonds are ruptured, the fragments of the original complex molecule are shielded electrostatically by the dielectric and are free to move in the liquid medium. This process may continue until the whole solid mass is dissolved or dispersed in the original solvent. That such a process may well have an important part in determining both the nature of the plastic state of coal and the yield obtained on distillation appears self-evident.

The above considerations receive additional support from the work of Fischer, Bähr, and Sustmann [13] on the distillation of coal under pressure of its decomposition products. These investigators showed that a non-coking coal would yield a coherent caked residue if so heated. The increased pressure decreases the rate of distillation of the volatile products of the pyrolysis and therefore affords time for greater solvent action than at atmospheric pressures.

The nature and amount of the "primary" products of thermal decomposition of coal must necessarily depend on the chemical nature of the coal itself; they are of importance not only in determining the coking, or plastic stage, of coals, but also from the point of view of the source of the compounds obtained in the tar and gas resulting from carbonization. As has already been pointed out in earlier paragraphs, coals contain carbon, hydrogen, and oxygen combined in highly complex structures. The work of Weiler [6] in a study of the halogenation of coal indicates that, for the particular coal studied, over 90% of the reaction of bromine and coal at 30° and 64°C is by substitution, and indicates relatively little unsaturation and the presence of considerable amounts of active hydrogen. This last fact, when considered in conjunction with the data of Juettner and Howard [12] on the composition of the gases obtained in high vacuum distillation of the same coal, suggests the source of the hydrocarbon gases obtained in normal carbonization of coal. Juettner and Howard found much higher proportions of hydrogen in the gas obtained under conditions of distillation where secondary decomposition in the gas phase was minimized than under the conditions prevailing in normal carbonization where gas once evolved from the coal may suffer many collisions with other gas molecules and the coal before being removed from the retort. If it is assumed, on the basis of the data obtained in the high vacuum work, that one of the early effects of heat is dehydrogenation of complex pyrolytic products of coal, the hydrogen liberated may react with alkyl side groups yielding simple gaseous

hydrocarbons or may react with unsaturated gaseous products of decomposition, and therefore hydrogen would not appear in large proportions in the gas until such reactions were no longer possible. This suggested mode of formation of the gaseous hydrocarbons obtained in normal carbonization practice is supported, in part, by the fact that hydrogen is not found in large amounts in the gas from coal until evolution of tar practically ceases, and, in part, by the increasing ratio of hydrogen to methane in the later stages of the carbonization.

Consideration of the effects of increasing severity of thermal treatment on the nature of the products obtained from coal [14] suggests that the origin of the aromaitc compounds found in coal tar is the "aromatic" nature of coal itself. The mildest type of pyrolysis is assumed to be that occurring in the presence of a solvent at low temperatures. Pictet and collaborators,[15] in a study of the products obtained on extraction of a coal with benzene at 80°C, and Hofmann and Damm,[16] in a similar study using pyridine at 115°C, isolated and identified many individual compounds, most of which contained one or more six-carbon rings although none of the compounds were simple aromatics. Several of the compounds isolated were of relatively low molecular weight and would have vapor pressures of several atmospheres at temperatures below that of active gaseous thermal decomposition. Below this temperature, the work of Juettner and Howard [12] shows that no appreciable yields of condensable products are obtained and therefore supports the hypothesis that the solvent extracts represent products of thermal decomposition. From these data we may conclude that the first products of pyrolysis of coal contain nuclei similar to those shown to be present in coal by a study of the products obtained by reaction with simple chemical reagents. Distillation at 450°C and 20 mm pressure yields many of the same individual compounds found in the extract obtained at lower temperatures, but still no simple aromatic hydrocarbons.[17] That the aromatic hydrocarbons are first formed between 450° and 600°C is indicated by the study of low temperature tar reported by G. T. Morgan and collaborators,[18] who isolated many aromatics from a tar prepared at about 600° C. It seems reasonable to assume that these aromatics result from dehydrogenation of compounds containing the six-carbon ring similar to those isolated in the solvent extract and vacuum tar obtained at lower temperatures. The higher proportion of simple aromatic compounds in high temperature tar would, therefore, be the natural result of more extensive dehydrogenation and

cracking. A more complete and satisfactory explanation of the origin of the compounds found in coal tar must await a systematic study of some single coal using all the methods of study described in the preceding paragraphs. This is an important part of the program of the Coal Research Laboratory. It may be pointed out that, for a complete understanding of the mechanism of thermal decomposition, or coking, of coal, a knowledge of the heats of distillation under the various conditions of pyrolysis is highly desirable.

Combustion

Many of the same factors that have been discussed in connection with the coking process are also of importance in the combustion of coal. Several stages in the combustion process may be recognized. When raw coal is charged into a furnace, the first stage may be designated as the heating up stage, followed by a period during which volatile products, including moisture, are distilled out of the coal, and finally there is a period during which the residue burns on the grate, or in suspension. Published data on the relative importance of these stages in determining the overall rate of combustion are not available.

It may be assumed that the first two stages take place concurrently and largely precede that last stage, since the evolution of volatile matter must prevent the oxygen of the surrounding atmosphere from reaching the surface. A knowledge of the chemical nature of the coal used, and particularly of the mechanism of its thermal decomposition, should help in understanding the initial stages of the combustion process, since, as discussed in the preceding section, the character of the residue depends on the mode of thermal decomposition. The time required for heating the coal and for elimination of the volatile matter are unknown functions of the thermal conductivity of the coal, its specific heat, the size of lump charged, the heat of devolatilization, and the temperature of the fuel bed. The size of lump charged is undoubtedly of more importance for non-coking coals than for coking coals, since the latter fuse at relatively low temperatures and the lumps of coal lose, thereby, their physical identities. In view of these considerations, it may seem surprising that data are not available for different non-coking coals giving the time of devolatilization and the time of heating to different temperatures as a function of size of lump. This may be due in part to the fact that both the size and shape of the coal affect the rate at which combustion air may be supplied to a

fuel bed, which in any particular case may be the factor determining the overall rate of combustion.

The final stage of the combustion process is a heterogeneous reaction between the oxygen of the air and the carbonaceous residue remaining from the initial stages. In any reaction of this general class, two different types of phenomena are involved: first, the diffusion process whereby the reacting gas reaches the surface and the reaction products leave the surface; and second, the chemical reaction at the surface. The overall rate of reaction is determined primarily by the slower of the two processes. Since the temperature coefficient of chemical reaction is so much greater than the temperature coefficient of diffusion, it is to be expected that, at the high temperatures prevailing in normal combustion and in part due to the exothermic nature of the reaction, and controlling factor in this final stage of combustion is the rate of diffusion of oxygen to the surface.

Several workers [19] have calculated rates of combustion on the assumption that the rate of diffusion of oxygen to the carbon surface and of the products away from it govern the speed of the process. With the help of certain assumptions, equations may be derived which, although rather unwieldy, give qualitative agreement between observed rates of combustion and the important variables, temperature, partial pressure of oxygen, air velocity, and size of particle. The lack of quantitative agreement between the calculated and observed rates of combustion may well be due to the uncertainties of the values of certain physical constants at the high temperatures involved. Mayers,[20] in a critical review of the work in this field, has developed an empirical equation which is based on the experimental data of Smith and Gudmundsen [21] and of Tu [22] on the combustion of carbon and which is not in conflict with any of the basic theoretical considerations proposed. This equation states that the rate of combustion is proportional to the partial pressure of the oxygen, to some power between 0.5 and 1.5 of the absolute temperature, to the velocity of air flow raised to the 0.4 power, and to the radius of the particle of carbon being burned. In view of the fact that use of the equation should be limited to combustion conditions not essentially different from those used by Smith and Gudmundsen, the proportionality factors will not be given here.

In formulating any diffusion equations, it is important to know the nature of the surface reaction. If CO is the primary product of reaction, two molecules of gas must leave the surface for each oxygen

molecule arriving and thus a "wind" may be visualized as originating at the surface. On the other hand, if CO_2 is the primary product, no such condition will arise. The work of Rhead and Wheeler [23] has shown that neither of these reactions is the primary one. When oxygen is admitted to a fresh carbon surface at high temperatures, a complex solid oxide of carbon, C_xO_y, is first formed, which then dissociates into CO and CO_2 in a ratio increasing with increasing temperature. That the first step in the reaction is formation of a solid oxide is supported by later work of Langmuir,[24] and by very recent work of Sihvonen [25] and Meyer.[26] It has been suggested by Meyer that, ignoring the formation of the oxide complex, the mechanism of combustion of graphite below 1450° may be represented by the equation

$$4\,C + 3\,O_2 \rightarrow 2\,CO + 2\,CO_2,$$

and, above this temperature, by a similar equation

$$3\,C + 2\,O_2 \rightarrow 2\,CO + CO_2.$$

Meyer's suggestion is based on data obtained by use of a low pressure technique, with an estimated probable uncertainty of approximately 30%. If the mechanism proposed above is accepted, the results of Rhead and Wheeler, which showed a ratio of CO to CO_2 continuously increasing with temperature, may be accounted for by assuming subsequent reaction of the O_2 and CO in the gas phase and of CO_2 and additional carbon.

A complete discussion of the chemical aspects of the combustion process of coal would necessarily include consideration of many additional factors: such as, catalytic influence of the ash; ash clinkering; film formation of ash at the surface; possible catalytic or inhibitory effects of moisture or other products of combustion; the effects of nitrogen, sulfur, and other elements which may directly enter the combustion process itself; etc. The data for evaluating the effects of these different factors are not available. To secure such data in a form that their significance might be clearly evident represents an extremely severe task for the experimental scientist.

*Gasification**

Chemically, the gasification of coal is a process analogous to com-

* The following discussion will not include gases obtained in the carbonization of coal, whose composition will obviously depend on the chemical nature of the coal and on the mode of thermal decomposition.

bustion. In this case, however, the reactions are endothermic and are normally carried out at temperatures lower than those that prevail in combustion. The reactions to be considered are the steam-carbon (coke) reaction to produce hydrogen and carbon monoxide and the carbon dioxide-carbon (coke) reaction to produce carbon monoxide. The heats of these reactions are fairly well determined for graphite, but are known only approximately for conditions of actual practice where cokes of varying composition are used, and for a complete understanding of the gasification processes, they need to be redetermined.

Due to the lower temperatures, it is to be expected that the rate of the surface reaction will be more important in gasification than in combustion and also of relatively greater importance than the rate of the diffusion process. This is recognized by the industry by the development of "reactivity" tests for determining the suitability of cokes for gas-making, since a change in the properties of the material will affect primarily the rate of chemical reaction at the surface. While certain of the experimental methods proposed [27] have demonstrated their usefulness, it may be pointed out that in none of these methods can the surface reaction factor be evaluated separately from the diffusion factor.

The reaction between CO_2 and carbon has been shown to be of the first order [27b,f,28] so that if concentration gradients at the surface are established due to diffusion effects, the measured rate of reduction of the CO_2 will not be the true rate for the temperature and pressure determined at a distance from the surface. Mayers [29] has recently reported a study of this reaction at temperatures ranging from 850° to 1300°C at one atmosphere pressure using an experimental technique which permits direct measurement of the rate of reaction at the surface. His results show that diffusion effects may reduce the apparent rate of reduction of CO_2 at 965°C to less than one-quarter of the rate of that obtained when diffusion effects are excluded. The first stage in the reaction appears to be a simultaneous reduction of CO_2 and formation of a surface oxide complex, in accord with the work of Broom and Travers [27a] and the low pressure work of Langmuir,[24] and which, at temperatures below about 950°C, may be represented by

$$C + CO_2 \rightarrow CO + (C\dot{-}O)_{\text{solid}}$$

The data obtained by Mayers indicate that above this temperature the solid carbon-oxygen complex decomposes as rapidly as formed and it is suggested that the reaction then becomes

$$C + CO_2 \rightarrow 2\,CO.$$

Similar data on the reaction between steam and graphite are not available, but it may be assumed that a surface complex is likewise an intermediate step in this reaction. The importance of the rate of the surface reaction in gasification processes may well account for the greater effectiveness of catalytic agents [30] than in combustion where the rate of diffusion is the controlling factor since the surface reaction is so much more rapid due to the higher temperatures. This would suggest that the various unstudied factors mentioned in the last paragraph of the section on combustion may be of even greater importance in gasification.

Summary and Conclusion

A brief review has been given of the chemical nature of coal, and certain chemical aspects of the utilization of coal for hydrogenation, coking, combustion and gasification have been discussed.

The present knowledge of the chemistry of coal utilization is extremely incomplete. Need for additional work on the fundamental chemistry of coal and its reactions is emphasized. The engineer has achieved much in coal utilization with the limited knowledge of the nature of coal itself at his disposal. Can we not look for still greater achievements as more is learned about our most important chemical raw material, coal?

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Discussion

H. H. Lowry (preceding paper): The paper that I have this morning is not a paper describing new uses of coal or new processes. I have attempted to review some chemical aspects of coal utilization and I hope that the paper will call attention to the fact that in coal utilization we have a field which needs the chemical engineer very much. Coal, really, is our most important chemical raw material in every field of utilization, coal must undergo a series of chemical reactions to reach the end sought. In the past two decades there has been a very considerable increase in the efficiency gained through the use of coal.

Chairman Marshall: Mr. Lowry's paper is now open for discussion.

J. R. Withrow: All of us, I believe, are enthusiastic about the developments in the hydrogenation of coal, particularly the things we have heard about from Europe. Certainly, anyone who has had the opportunity of seeing the great mines and the laboratories for research along this line would be enthusiastic. Years ago there was a chemist in the United States by the name of Gustav Hendrix, of St. Louis. Some of us remember his work, most of which was published in the Compte Rendus (Paris). The former president of the American Chemical Society, Edgar F. Smith, was a great believer in working on atomic weights, starting with a hundred pounds of material. Gustav Hendrix, on the other hand, followed the theory that one should work with minute amounts of material. In coal research all of us understand, especially engineers, the importance of working on large amounts but it seems to have remained for Dr. Lowry to take up the theory which was followed by Hendrix to work with atomic weights and with small amounts. I want to say, for those who have not had the opportunity of seeing Dr. Lowry's laboratory, that it is a revelation of the finest type of physio-chemical work, micro-analysis, and micro-distillation. We are not, perhaps, interested in going into

this, but we should be aware of the fact that some of these things to which Dr. Lowry is calling attention, while they may not have any immediate practical application, are undoubtedly the foundation on which engineers in the future build their work.

I would like to ask Dr. Lowry in what portions of the United States we have coal similar to that which they use in Germany. I suspect we do not call that material coal in this country.

H. H. LOWRY: You mean the coal used for hydrogenation? I do not believe we have any exactly like theirs. That is a brown coal. We have lower ranges than bituminous, lignites, but they are quite different, I believe, from the German brown coals. The American coals are susceptible to hydrogenation. I believe the Standard Oil of New Jersey have prepared gasoline from certain American coals in their survey of hydrogenation; and Professor Busline, at the University of Washington, has been studying hydrogenation of American coals and has published much of his work.

CHAIRMAN MARSHALL: Is there any other discussion of Dr. Lowry's paper? I should like to draw your attention to the fact that Dr. Lowry has included a very excellent bibliography with his paper.

The next, and final paper of the program is "Acetic Acid Dehydration," by Donald Othmer, of the Polytechnic Institute, Brooklyn, N. Y.

ACETIC ACID DEHYDRATION

By DONALD F. OTHMER *

Acetic acid has always been the most abundant and most useful of the fatty acids. Like its other near homologues, it has a strong affinity for water; not so strong as in the case of formic perhaps; but of considerable interest because of the large amount of technical skill which has been expended in devising methods for overcoming this affinity. The anhydrous, or glacial, acid is necessary in some important uses, such as the manufacture of cellulose esters. The dehydration of aqueous solutions is important not only in the several methods for producing the raw material, but because of the greater or less dilution which always occurs to the large amount of acid cycled in cellulose processing, it is of prime importance in the manufacturing plants which use the largest tonnage. The present purpose is to classify by types some of the methods proposed and in use for removing part or all of the water from an acetic solution. Only a few of the many processes available can be discussed; but the general theories will be compared.

Chemical

The oldest process for the production of anhydrous acetic is the neutralization with an alkali, evaporation of the water and drying of the solid acetate salt, decomposition of the acetate with sulfuric acid and distillation of the acetic from the non-volatile sulfuric. Theoretically an anhydrous acid may be obtained in this manner, but in practice a crude material averaging about 80% is obtained when lime is used as the alkali; and this is subsequently refined. Schaack and Calvert, U. S. 1,765,318 decompose the calcium acetate with sulfuric, and filter off the gypsum formed, leaving a mixture of sulfuric and acetic acids which is suitable for certain purposes. An analogous process to the salt conversion is the esterification with methanol or ethanol, the removal of water by distillation, and the subsequent hydrol-

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ysis and separation of the acid and alcohol (von Retze, U. S. 1,647,676). Lichtenthaeler (U. S. 1,660,756), forms the ester in the presence of hydrate forming salts which simultaneously absorb the water.

There are other chemical processes involving a neutralization or combination with various organic materials, such as Othmer (U. S. 1,897,816), which combines acetic with triethanolamine in much the same general process as has been used for absorbing H_2S and other weak acids from air. The water is first driven off by heat, and the acetic acid is then removed by decomposing the triethanolamine complex at a somewhat higher temperature. Dreyfus (U. S. 1,851,664) reduces the acetic to acetaldehyde, removes the water and oxidizes the aldehyde into concentrated acid.

Materials which will absorb the water as hydrates, for removing the water in a chemical compound, have been used as well as others showing a preference for the acetic in acid salts which are readily decomposed (Brit. 281,827). The chemical methods merge into the physical ones, especially extraction, with such processes as Schwaebel and Schleicher (U. S. 1,766,404), where an unstable salt of an organic base increases extractive efficiency.

Also included in such processes would be the important one of the production of acetic anhydride via sodium acetate and sulfur chloride, or other process starting with dilute acetic such as the one involving the ethylidene diacetate stage. In a cellulose acetate plant where several times as much acetic as the amount of anhydride used for acetylation must be used as a solvent or diluent, and in the best practice, all finally discharged as a dilute acid of from 25%-40%; it is apparent that all of this dilute acetic cannot be converted to anhydride without an oversupply of the latter.

In general, these chemical methods are of minor importance except in the wood chemical plants which have not installed modern processes, and, as related to anhydride. The complications of equipment and handling, the comparatively poor yields, and the waste of chemicals used are the principal disadvantages when compared with the physical processes in modern favor.

Distillation

The operation most often used for separating two liquids is distillation, and in most cases, rectification. The theory and practice is

fairly well understood for binary mixtures and is based on the Vapor Composition curve, which defines the composition of vapors arising from a boiling mixture of a given composition. Figure 1 is the vapor composition curve of acetic acid and water, and the closeness of the curve to the 45° line, and therefore the small difference between vapor and liquid composition, illustrates the difficulty of the separation by rectification. It is possible, however, to accomplish a "frac-

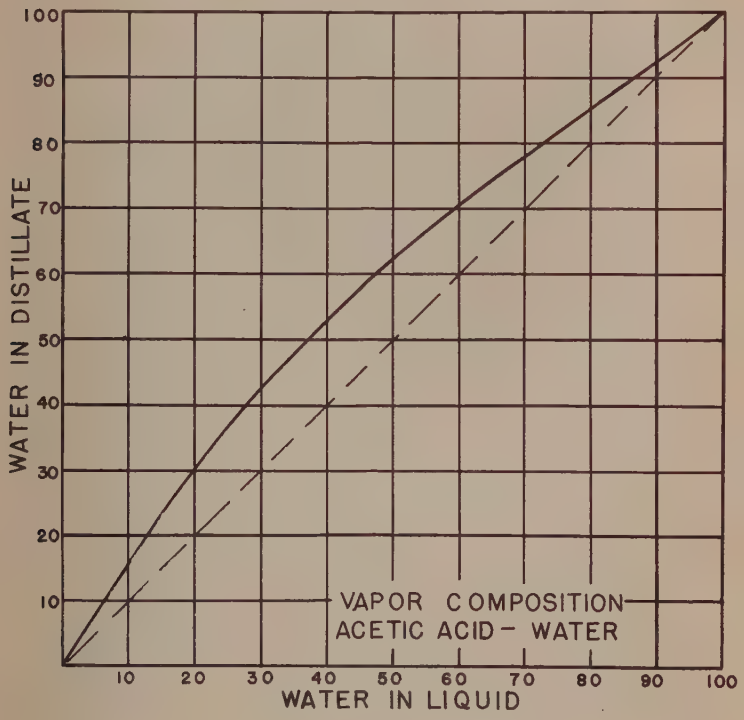

FIGURE 1

tionation" of more or less efficiency; and the 28%, 56% and 65% strengths of acetic on the market represent these fractions obtained in the refining of an anhydrous grade from the 80% crude from the lime-sulfuric method described above. No distilling column, probably, has ever been operated turning out acid free water at the top and

glacial acid at the bottom although this would be possible theoretically; and calculations show that the column would not have to be of prohibitive height if modern, efficient, bubbling caps were used. The heat cost would be excessive, however, because of the large reflux ratio which would have to be used.

The difference of the boiling points, 118.5°C. for acetic and 100° C. for water, is no less than that between other materials which are satisfactorily separated by rectification. The closeness of vapor and liquid compositions may be regarded as due to the affinity between water and an acid which produces constant boiling mixtures, and makes entirely "abnormal" the vapor pressures of mixing with water of the mineral acids, as well as formic, and other strong organic acids.

Resort may therefore be made to a trick of distillation technique first described by Sidney Young some thirty years ago in the production of absolute alcohol. The theory is more simple in the case of acetic acid and water than with alcohol and water, and rests on the simple steam distillation principle which forms the basis for experiments in all courses of elementary physical chemistry.

The vapor pressure of a mixture of two liquids which are substantially mutually insoluble is, at any temperature, approximately equal to the sum of the vapor pressures of the individual liquids taken alone. Thus, the boiling point, *i.e.*, that temperature at which the vapor pressure equals the total pressure operating on the system, will be considerably lower than that of either of the liquids alone. This simple relationship does not hold for liquids which are miscible; and for this reason, if an organic liquid which is miscible with anhydrous acetic acid but substantially insoluble in water is added to aqueous acetic, and the mixture distilled, there will be a tendency for the water and organic solvent to distill together at a lower temperature while the vapor pressure of the acetic acid will not be affected to so marked a manner. Rectification is the successive and progressive distillation of liquids in such a manner as to separate the material of the higher vapor pressure or lower boiling point. A rectifying column will thus separate the water-solvent mixture from the acetic acid more easily than it would separate the water alone.

Several requirements for a liquid to be used as a withdrawing agent for removing water from acetic acid have been enumerated by Clarke and Othmer in U. S. patent 1,804,745:

1. It must not react with acetic acid, nor be decomposed, when boiled with the latter, into impurities which would contaminate the acid.

2. It must be available cheaply in large quantities.

3. It should boil at a lower temperature than acetic acid and thus be readily and completely separable from the latter by distillation.

4. It must form an azeotropic mixture with water vapor.

5. Its miscibility with water should be low.

6. It must cause the concentration of acetic acid in the watery layer of the distillate to be always lower than that of the aqueous acetic acid which is being concentrated,—such difference in the concentrations being as large as possible.

7. The latent heat of the solvent and the composition of its azeotropic mixture with water-vapor should be such that the amount of heat required for vaporizing a unit amount of water (in the azeotropic mixture) should be as low as possible.

8. The distribution ratio of acetic acid between water and said auxiliary liquid, or in other words, the ratio of acetic acid in the water to that in said liquid when the two liquids containing acetic acid are in contact (say in superimposed layers) should be low.

No mathematical or graphical method, comparable to the McCabe and Thiele method for analysis of the rectification of more usual binary mixtures, has been devised for predicting the performance of a column working with a withdrawing agent; and, in all probability, none of any general usefulness can be devised because of the interrelation of some of the controlling factors with the particular design of column employed.

In practice, it has been found possible while utilizing a withdrawing liquid, to operate a distilling column in much the usual manner but with one condenser only at the top, which spills condensate into a gravity decanter. Advantage is taken of the difference in specific gravity between water and entraining liquid; and all of the latter, after separation in the decanter, is returned as reflux, the water being discharged substantially acid free. With such an arrangement, the reflux "ratio" is automatically fixed to the amount of entraining liquid brought over the head of the column for a given amount of water. Ricard and Guinot (U. S. 1,862,706) describes this method; but the method itself was in use by many others long before the date of this

patent. Distillation using withdrawing liquids under several atmospheres pressure has been suggested, Keussler (Canadian P. 268,241); but, from considerations which follow, this will be seen to offer no advantage in the usual case.

The thermal efficiency of such a process is dependent largely upon the relative vapor pressures of the solvents employed in comparison

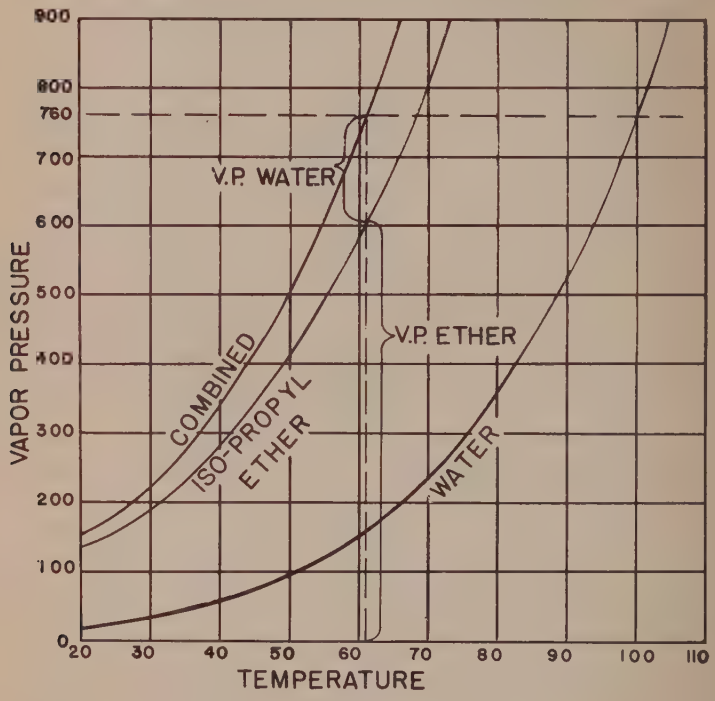

FIGURE 2

with that of water. Thus, if isopropyl ether is considered (Davidson and Schaefer, Can. 324,125), the vapor pressure is so much higher than that of water that the proportion of water in the vapors is very small. From Figure 2, and the molecular weights of isopropyl ether and water, may be calculated that only 1 gram of water will be carried over for 20.9 grams isopropyl ether. Thus a distillation system using isopropyl ether as a withdrawing liquid will return approximately 20.9

grams of isopropyl ether as reflux against 1 gram of water separated from the acetic acid. If the dilute acid was of twenty-five per cent strength, for example, this would be multiplied by three to give 62.7 grams isopropyl brought over the top per gram of acetic recovered.

With ethylene dichloride as a withdrawing agent as covered by U. S. 1,804,745, the method of summing vapor pressures, and converting from relative moles to relative weights gives a ratio of approximately 11.9 grams ethylene dichloride per gram water. The important consideration is that of the amount of heat required for the separation; and if the weight of entraining liquid is multiplied by the respective latent heat, it follows that 1425 calories of heat are required to vaporize the isopropyl ether required to bring over 1 gram of water as compared to 920 calories with ethylene chloride. Neither of these takes into account the heat required to bring over the 1 gram of water itself—which in both cases may be regarded as approximately 540 calories.

While this calculation shows that ethylene dichloride has so much higher thermal efficiency than isopropyl ether for removing water from acetic acid, other materials have considerably greater efficiency in this regard. Of the dozens known which satisfy the requirements enumerated above, all of them are the subject, either of granted patents, to a half-dozen inventors or assigners, or of patent applications controlled by the author personally; and several of the latter indicate the possibility of concentrating acetic acid more cheaply than by any method now in industrial use.

This discussion has included merely the removal of water by the distillation process; and if the process is discontinuous or batch, the acetic is finally completely dehydrated in the pot and contains the withdrawing liquid, which must be removed by further rectification in the usual manner as a separate fraction. The acetic is then finally distilled over free of both water and dehydrating agent. In the continuous operation, which is much to be preferred here, as in most other distillation methods, the column is simply charged with sufficient entraining liquid to accomplish the dehydration at the top of the column, without getting into the pot, wherein is maintained anhydrous acetic acid. The lower section of the column is thus used in the usual operation of separating acetic from a lower boiling material—the entraining liquid. The dilute acid feed is introduced at some point into the side of the column; and the whole proceeds as a satis-

factory machine separating substantially water free acid at the bottom from substantially acid free water at the top. The only remaining factor to allow the process to proceed indefinitely is the fact that the water discharged from the decanter will be saturated with the entraining liquid and would ultimately remove all of it from the column. This is taken care of in one of two ways (1) if its solubility in water is low and the material is cheap, the water is run to waste; and fresh withdrawing liquid is introduced into the column from time to time to balance the loss; (2) the water is run into the top of a second small distilling column which strips it of the withdrawing liquid and discharges the withdrawing liquid in substantially the same mixture with water vapor as that issued from the main column. This vapor mixture from the stripping column may then be passed to the same condenser as that from the dehydrating column, and the condensate is indistinguishably mixed in passing to the decanter.

Othmer, in U. S. Patent 1,917,391, illustrates the arrangement of equipment for the continuous dehydration of acetic acid using ethylene dichloride as a water removing agent, and details the controlling factors in the design and operation of such equipment. Figure 3, reprinted from the patent, illustrates in diagrammatic form the relative arrangement of the pieces of equipment. A further modification described in this patent allows the preliminary separation of salts and other non-volatile waste material in dilute acid that is being recovered from such processes as the acetylation of cellulose. The dilute acid is pre-evaporated in the supplemental still pot; corresponding to the "tube still" of petroleum distillation; and the mixture of water and acetic vapors is fed into the side of the column. Waste solid material remains behind in this pre-evaporator without entering the column. Salts of limited solubility in glacial acetic, if allowed to enter in a liquid feed, might suddenly precipitate out in the column at that plate where the last of the water is removed. Pre-evaporation removes the cause of this nuisance; and if the pre-evaporator is correctly designed, salts can be discharged from it without the necessity of shut down of any part of the system.

As mentioned above, no method for calculation and prediction of the number of plates required in a distilling column for this separation has been developed; and different liquids, even of very nearly the same boiling point exhibit widely different separating efficiencies in the same type column; or, indeed, may even bring acid of a very con-

siderable strength over the head of the column. (The difference should be noted between "separating efficiency" which governs the ease of separating substantially acid free water from substantially water free acid, and "thermal efficiency" which governs the amount of heat required to accomplish the separation.) The last mentioned

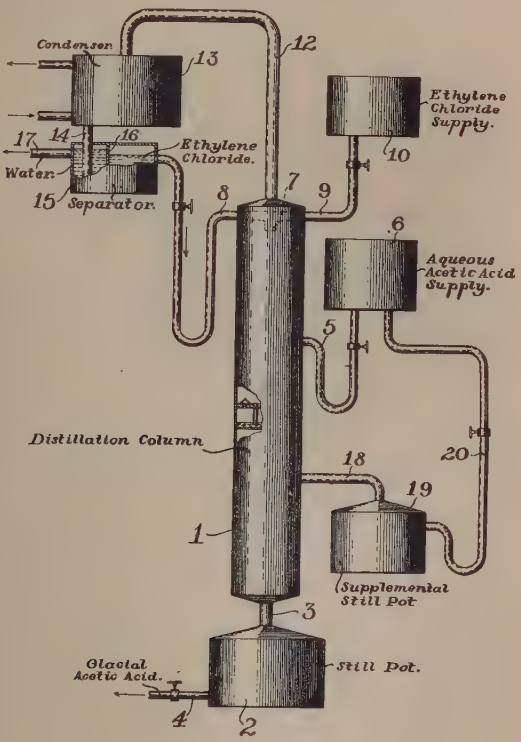

FIGURE 3

patent specifies forty plates as a suitable number for the ethylene dichloride distillation referred to; and in general, depending on several physical properties of the liquid used, of which boiling point is only one, the number of plates required for satisfactory separation may vary between about fifteen and sixty.

Many modifications of this method of distillation in the presence of withdrawing agents have been proposed, an interesting one is that

of the Wacker Gesellschaft using butyl acetate (B. P. 298,137). The closeness of the boiling point of the butyl acetate to that of the acetic prevents the separation of the withdrawing agent after the water has been removed; and more water is then added to separate the withdrawing agent from the acid.

While this method of removing water from acetic by the use of withdrawing agents is usually loosely referred to as "azeotropic distillation," it is more nearly a "steam distillation" in the usual sense. A constant boiling mixture giving a distillate separating into two layers is termed a "heterogeneous azeotrope," and is quite different from the more usual homogeneous type, ordinarily referred to simply as "azeotropic."

The term "azeotropic distillation" might more correctly be applied to a process such as that of Ricard and Guinot (U. S. 1,839,932 and several others) and several others, in which, after separating acetic from water first by extraction and then by a distillation step, the acetic acid is separated from the extracting solvent by the use of an additional liquid such as a petroleum fraction boiling between 114° and 116°C which forms a homogeneous azeotrope with acetic acid boiling at 100°C at which temperature it can be removed satisfactorily from the extracting solvent. In this involved process, water is then added to separate the acetic and petroleum fraction into two liquid layers, and the acetic layer is finally completely dried in a final distillation operation.

Extraction

On December 18, 1883—fifty years ago—almost to the day, Dr. Theodor Goering filed his application which resulted in German patent number 28064, entitled "Process for the Production of Concentrated Acetic Acid and Acetates from dilute aqueous Solutions by means of Extraction." This patent and the work it represents are interesting because of the number of people who have since gone to the labor of determining the same thing. It developed the field which has since been worked in by many others, sometimes without knowledge of the earlier work. Indeed, by specifying the distillation of such an extracting material as ethyl acetate from dilute acetic, it indicates that Goering was familiar with or, at any rate, accomplished so called "azeotropic" distillation, many years before Young dehydrated alcohol by distillation in the presence of a third liquid.

A translation of parts of the patent specification is helpful to an

understanding of the process of extraction: "Acetic acid is, for a time, mechanically transmitted to another liquid from which it can easily be separated. . . . The temperature is of little importance. . . . If, for instance, water containing acetic acid is brought into contact with ethyl acetate, there will be a division of the acid present between the two liquids, depending on their respective volumes. . . . If an entire absorption of acetic acid is required from the liquid which has to be extracted, the contact must be conducted systematically, that is, a counter flow is arranged between the two liquid layers within the extraction vessels, no matter whether only one or several combined vessels are employed. In this manner, a degree of saturation in the extraction solvent will be obtained that corresponds to the original concentration of the aqueous solution of acetic acid; and therefore a smaller amount of the solvent will be necessary. The liquor is exhausted of acetic acid, while dissolving a certain quantity of solvent, which will be recovered by distillation. . . . In the production of concentrated, acetic acid, low boiling esters are employed as extraction solvents. In the distillation which follows, these are removed with moderate diphlegmation, nearly free of acetic acid, while the acid rests as remainder."

Dr. Goering at that early date described the principles and practice of the recovery of acetic as used in several large plants today. He even specified and gave the characteristics of one of the solvents now used. Two further modifications were described: one the subsequent extraction of the acid from the solvent with pure water, thus leaving most of the impurities in the original aqueous phase, and those extracted by the solvent, in the solvent phase. A second was the addition of salts to decrease the relative solubility of acid in the solvent as compared to its solubility in water; and of other salts to combine with the water dissolved with the acid by the solvent. The purification method using the solvent substantially as a filter for removing all kinds of liquid and solid impurities has never been used so far as is known simply for separating foreign materials from aqueous acid; although the purification so obtained by extraction and distillation is of practical importance wherever the method is used. The addition of salts has been mentioned in many subsequent patents, but the advantage so gained is usually more than offset by the complication and cost of recovering the salt for reuse. A modification patented by Ricard and Guinot (U. S. 1,860,553) and by

Dreyfus and Haney (U. S. 1,696,432) makes use of a second liquid such as a hydrocarbon in a mixture with the solvent. This reduces the solubility for water of the solvent layer, and therefore secures a stronger acid.

Suida (U. S. 1,624,810), Martin (U. S. 1,717,719), von Belatin (British 20,125), and many others have secured patents on modifications of this process with the same or different solvents, while Brewster failed to obtain patent protection in this country on the use of ethyl ether in the same process. Brewster's system has been, and is, used in this country and abroad with ethyl ether or isopropyl ether depending on the relative costs of the two solvents, and the temperature of the cooling water available. Von Belatin wanted to produce a strong edible vinegar and preferred the use of ether because it carries through the aromatic flavors associated with vinegar, while leaving the water behind.

Ricard and Guinot (U. S. 1,860,553), clarify Goering's distillation step and claim the use of lower esters, first as extracting agents, and then as azeotropic withdrawing agents.

Liquid-liquid extraction is a unit operation of chemical engineering, the mechanics of which have not been as well investigated as in many other unit operations. The prediction of performance is based on different physical factors than those governing rectifying column calculations; but the general method of approach is, of course, the same since both are methods based on diffusional relationships. Various published and unpublished methods of mathematical analysis which have been suggested depend on simplifying assumptions and involve greater or less error. A very considerable field of theoretical and practical interest is being opened up in the increasing use of liquid-liquid extractors not only for acetic acid concentrations but in other fields as well.

Liquid-liquid extraction depends on a diffusional process between the particles of two liquid phases rather than between the particles of a gaseous and a liquid phase as in the case of rectification. In both cases, it is necessary to apply mechanical energy to intimately contact the particles of the two phases; then the particles are usually allowed to separate into the two respective phases; after which, the process is repeated again and again. In distillation and rectification, the mechanical energy is immediately available at no cost for as many steps or "plates" as desirable by the simple expedient of building

up in the still pot a vapor pressure above that of the rest of the system. The vapors are then allowed to perform the work of agitation and mixing which they do with a very high degree of efficiency, on the plates of the column as the vapor phase expands from the higher pressure of the still pot to the lower pressure of the condensor. No such simple and automatic mixing method is available in the case of counter current liquid extraction; and, in general, outside mechanical energy has to be supplied to the extracting system in order to break up the liquid masses into small particles, which by diffusion can come to a state of substantial equilibrium within a short time. It is interesting to note in this connection that while a practical plate in a distillation column never exceeds 60-75% of the efficiency of a "theoretical" plate, i.e., one in which every particle of vapor comes to equilibrium with every particle of liquid, it is not impossible for a section in an extraction battery to exhibit over 100% of the theoretical (because of the settling action after agitation) and substantial equilibrium in each section can usually be readily obtained by properly designed agitating sections.

Various types of extracting devices have been used for systematically contacting in counter flow the solvent layer with the aqueous layer which originally contained all of the acid. These may be roughly classified by types, as: (1) individual cell, (2) mixer-baffle, (3) droplet, or film. The individual cell type is simply an enlargement of the principle of a series of separatory funnels which are shaken and allowed to settle; in which the aqueous acid layer is drained off of number one, passed to number two, is there drained off and passed to number three and thus through the higher numbers becomes progressively weaker in acid. The solvent layer in its turn passes from the higher numbered cells through the lower, each time being completely decanted, and becomes progressively stronger in acid; finally discharging from number one as close to equilibrium with the aqueous feed as may be obtained practically. In practice, the agitation and decanting steps are always done in separate vessels to prevent the necessity of a periodic operation, as would be obtained with the separatory funnel system.

This method, which is more elementary in principle than anything in distilling practice and compares only to a multiple unit spray gas washer, involves a considerable amount of tankage, piping, pumping and mechanical drives for an installation. There are many items of

equipment in a battery of, say, fifteen units, each of which requires an agitator and a decanter as well as a gravity or mechanical flow for one of the layers, and a mechanical flow for the second. In British Patent 307,868 is described one of the most practical arrangements of this mechanism, in which the lighter layer is allowed to flow from one decanter by gravity to the following, lower spaced, agitator; and the heavier layer is pumped by an air lift to the preceding, higher spaced agitator. Nitrogen or other inert gas is used in a closed system rather than air because of the corrosive action of air and acetic acid together on the usual materials of construction.

The mixer-baffle type extractor usually takes the form of a column with the aqueous acetic fed in at the top, and some solvent of low specific gravity, as ether, at the bottom. The two liquids flow in opposite directions because of the differences in specific gravity, but are alternately intimately mixed by a series of agitators, and allowed to separate by passing through a space filled with baffles. A representative of this type is that of Coahran (U. S. Patent 1,845,128). The analogy here is apparent to the usual plate rectifying column, in which the vapors in small bubbles, agitate the liquid on each plate and, subsequently, lose any entrained liquid in the vapor space between the plates. It is exactly comparable to gas washing or rectifying columns of the Bartlett-Hayward type in which the division into small particles is made possible by a mechanical rotor or sprayer.

The third general type is the so called droplet or film type extractor which depends for its action on the diffusion taking place between a droplet or film of one liquid rising or falling in a mass of another liquid. Usual practice is to fill a tower with two liquid layers: solvent of low specific gravity on top and aqueous acid below. Dilute acid is sprayed into the solvent layer near the top of the tower; and the droplets formed are allowed to settle down through the solvent layer to coalesce with the aqueous layer maintained at a constant level in the lower part of the column. Similarly, droplets of the solvent are allowed to settle up through the lower aqueous layer to the solvent layer floating on top. The action in exhausting the feed is thus seen to be a summation of the diffusion of acid through the walls of aqueous droplets into the body of the solvent, and of the washing action of the solvent droplets as they rise through the lower, aqueous layer. Several forces oppose the perfect action of such an arrangement, the most important probably is the tendency of the droplets

to coalesce during settling, and thus to increase to so large a diameter that the diffusion process cannot go to anything like completion within the time allowed during settling. One method of counteracting this disadvantage is to use a column filled with some form of packing shapes, and to depend on the droplets coalescing into thin films which run up or down the surfaces of the packing shapes in thin films bounded on one face by the bulk liquid of the opposite layer. Data are not available for comparing performance of the two modifications, the first of which is analogous to a "spray" distilling column and the second compares in its action directly with the usual packed column for rectification. The same tendency toward "channelling" is to be noted in this type of extractor as in the packed distilling column.

Extractor columns of the droplet or film type as high as 80 feet have been used in Europe to give the required amount of counter flow; and others of comparable height are in use in this country. In general, the height must be very considerable to secure efficient operation; and in some cases, this height has been secured in two or more sections placed side by side.

A second main class of extracting methods, the contacting of liquid with superheated vapor is even more nearly analogous in theory and practice to rectification technic. It consists in the passing of a superheated mixture of vapors up a column of the usual bubble cap type used for rectification, down which is flowing a solvent for one of the components of the vapor mixture having a sufficiently high boiling point to prevent volatilization. The process is an extraction rather than a rectification and is simply a thorough and countercurrent gas washing operation. Suida (U. S. 1,624,812, 1,697,738, 1,703,020, and others) developed this process in Europe and in this country primarily for the removal of acetic from pyroligneous; and due to the improvements made in this country has given a process of widespread use in the wood distillation industry. The basic principle, that wood tar oils decrease the vapor pressure or "hold back" the acetic acid from an aqueous solution, had long been known by wood distillers from experience in their distillations of wood tars. The disadvantages are a higher equipment and steam cost than the best of the cold extraction methods, and the fact that approximately 80% acid rather than the anhydrous is made. Another vapor phase extraction process, Schwaebel and Schleicher (U. S. 1,766,404), utilizes organic bases for vapor phase extraction.

Still a third type of extraction has been proposed (British 308,-210) which refrigerates the aqueous solution in the presence of a solvent cooled to about—25°C. The acetic acid is dissolved in the solvent and the water separated mechanically as ice crystals. Solvent is subsequently separated by distillation. This is one of the best of the several refrigeration methods proposed for taking advantage of the unusual freezing properties of mixtures of acetic acid and water.

The principal cost of operation of an extractor is mechanical power; of a distilling column, heat. A distilling column is a very inefficient heat engine; and in those cases where either an extractor *or* a distillation system using a withdrawing agent may be used, the operating cost would be tremendously in favor of the extractor. In general, of course, an extractor cannot be operated without an auxiliary distillation system which doubles the number of steps and the amount of equipment required. Nor can a simple extraction step produce dry acid, since the mixture of acetic acid with solvent, increases tremendously the solubility of water in the latter; and the subsequent removal of the solvent leaves an acid containing some water. The extractor is seen to be an efficient tool for cheaply effecting a rough separation of most of the water; but its use is also found to have some limitations; largely in the resulting complication of equipment and processes. In many methods, an extraction step first removes most of the water with one or more added extracting liquids which are subsequently separated from the dissolved aqueous acid; then a second added liquid is introduced and distilled to remove the water as a withdrawing liquid. The ideal arrangement would be the combination in one liquid of good extracting properties for a first step and good withdrawing properties for the second.

The balancing of these various factors to secure the most advantageous system depends on steam costs, equipment costs, amount and strength of the acid to be handled, and the resulting concentration desired, availability of various solvents both as to cost and patent licenses, cost and type of labor available. (The control of a recovery system of this nature demands intelligent operation). Obviously, the more complicated systems would be practical only on very large scale production; smaller operations cannot afford the expense of the fixed charges of the more involved processes. From what has been said above in regard to extraction versus distillation in the presence of withdrawing agents, it follows that extraction would not be econom-

ical—or possibly even not operative—with a solution containing only a small amount of water, and will become highly desirable below some limiting concentration, depending on the magnitude of these various economic effects in each case.

An improved extraction method utilizing known materials in more efficient methods has been recently developed.

Discussion

D. F. Othmer (preceding reading of the paper): There are several interesting aspects I would prefer to take up aside from the paper if I had time. One of these would be a thorough study of two or three processes of concentrating acetic acid; a study of actual plant operation; a discussion of the equipment involved; a discussion of the very interesting features of equipment design—chemical engineering equipment design for handling these various operations; a discussion of materials for construction of this equipment, and since many of these problems involve distillation equipment, a discussion of the differences of still construction, column design, column operation from the usual solvent or alcohol stills and columns and equipment of that sort.

Yet another would be a study of the economics of the industry as a whole, that is, some discussion of the curves of production, the curves of costs and a comparison of the costs of different processes in concrete detail. Another phase which has been of interest in the last year or so has been the phase of chemical engineering balances of materials and heats, the set-up of various types of calculations for the performance of some of these types of specialized equipment which are used in this industry, and the set-up of the material balances for estimating the efficiency of performance of this equipment would in itself be an interesting study and an interesting paper.

Or yet, if the work was in a final form, I might rather discuss this morning some rather newer processes which have been worked out in the last few months which seem to give an indication of low cost operation in comparison to any of the plants with which I am familiar. Unfortunately, for several reasons, I cannot talk on any of these items which I have just mentioned. Instead, I shall run through, briefly, a discussion of the representative methods into which the various processes may be classified. I shall not go into a

discussion of the various patents or a comparison of their merits, as these are listed in the paper.

CHAIRMAN MARSHALL: The paper is now open for discussion.

T. H. CHILTON: This was a very interesting discussion of the types of columns. There is one type, however, that I did not see mentioned in the paper—the sieve plate type column, which corresponds in construction and in operation to the sieve plate type of distillation column. I might also call to the attention of those interested in this subject a series of articles appearing in the magazine entitled "The Industrial Chemist for July, August and September of this year (1933), by T. G. Hunter and K. W. Nash, and also to a paper which the same authors presented at the World Petroleum Congress, which gives actual extracting efficiencies for both the typical sieve plate type and the typical packed extraction column.

CHAIRMAN MARSHALL: If there is no other discussion, the paper program will end.

PHENOLIC PLASTICS IN THE CHEMICAL INDUSTRY

By WM. H. ADAMS, Jr.*

During the past twenty-five years the production and utilization of the various types of so-called synthetic resins have been a very fertile field for many investigators. As a result there is now available an extremely diverse list of products based on these materials which touch many industries.

Of the hundreds of synthetic resins which have been suggested only a very few have achieved significant commercial development, either because of the lack of some fundamental property or because of excessive cost. Among the more important commercial types of resin may be listed [1,2] the phenol-formaldehyde condensation products, the urea-formaldehyde and the thio-urea resins, the polybasic acid polyhydric alcohol resins, the phenol-furfural products, the polymerized hydrocarbons, and a few others. Each of these resins has a field of utility in which its particular properties render its use desirable.

In the chemical industry there has been a considerable recent development in the use of phenolic type resins, particularly in corrosion resistant chemical plant equipment. This is due to certain properties of these resins which make their use under these conditions especially desirable. Such resins are hard and strong, and are excellent electrical insulators. They do not melt nor soften appreciably at moderately elevated temperatures nor are they injured even by prolonged exposures up to about 135° C. They do not crack with sudden temperature changes. Finally, they are extremely resistant to the action of moisture, most acids and solvents, many of the weaker bases, and numerous other chemicals, and are, therefore, capable of solving many problems in the handling of corrosive materials.

The resistance of phenolic resins to chemical attack has long been known, and was, in fact, noted by many of the early investigators.[3, 4, 5] It is, therefore, rather surprising at first sight to note that until recently there has been no significant development in the use of these materials in chemical plant equipment. Actually, however, the prob-

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lem was a rather difficult one, partly because of manufacturing limitations and partly because of the economics of the situation.

A very early idea was to use the solid phenolic resin, cast or molded to shape. The acid resistance of such products was excellent, but they were limited as to size and were fragile and easily broken. This brittle character of the pure resin led to the very early use of other materials in conjunction with them, to lend them strength and toughness.[1, 2]

Two general types of re-enforced resin products have been developed to fill the need for a stronger material. The first is the so-called "molding powder" which consists essentially of an admixture of resin and a fibrous filler, usually woodflour or asbestos. The powders are formed under heat and pressure in intricate molds. This process lends itself admirably to the quantity production of small parts, but for chemical plant equipment, where the size is large and the quantity limited, the cost of the molds is so excessive that the process becomes economically unsound.

The second type of re-enforced resin product is the so-called "laminated" material, which usually consists of layers of paper, cloth, or asbestos, impregnated with resin, and bonded together with heat and pressure between plates in a hydraulic press. This product is very tough and strong, but can only be made cheaply in a few relatively simple shapes, such as sheets, rods, tubes, etc. While tubes and a few other forms can be used directly as constructional material for pipes, towers, etc., the complicated apparatus needed by the chemical industry could for the most part be built up only by the hand fitting of small pieces. This process is too expensive to be generally applicable.

In addition to the economic limitations of these materials, there have been, until recently, chemical disadvantages as well. In the early days of the industry, the major emphasis was on a material for electrical insulation; when attempts were made to apply such grades in the chemical industry, they were found to be entirely unsuitable. Traces of acid could penetrate the mass and disintegrate the usually rather crude cellulosic materials used as fillers.

Recently, however, new grades of these products have been developed for chemical service which represent a marked improvement. This improvement was attained by the use of more resistant resin, purer types of cellulose and better manufacturing technique.

It should be emphasized that while these grades can be used with

a large number of acids, salts, solvents, and weak bases, they can in general be used only under moderate conditions of concentration and temperature. This is because even with the advances which have been made, it is still possible for strong hot chemicals to penetrate sufficiently to cause eventual deterioration of the cellulose. When used under the correct conditions, however, such products have an excellent life expectancy, and their strength, toughness, light weight, resistance

FIG. 1. Laminated phenolic resin pipe line in service in a chemical plant for the handling of dilute hydrochloric acid.

to rapid temperature changes and ready machinability combine to make them very adaptable materials from the design standpoint.

Among the types of equipment of this nature which have been made may be mentioned rayon spinning buckets, drying trays, pumps, towers, and tower sections, pipes and fittings, etc. Fig. 1 illustrates a laminated type pipe installation in hydrochloric acid service. Such pipe has been one of the major applications of this product to date.

The economic and chemical limitations of the conventional phenolic plastics as applied to plant equipment led to further research with these materials. Resulting from this study a new type of plastic

"HAVEG 41" IS RESISTANT TO		"HAVEG 43" IS RESISTANT TO
ACIDS	SALTS & OTHER CHEMICALS	Hydrofluoric Acid
Acetic, any conc.	Aluminum Acetate	Fluosilicic Acid
Fatty Acids	Aluminum Chloride	Hydrofluoric Acid Mixtures
Formic, up to 40%	Aluminum Oxalate	Fluorides
Hydrochloric, any conc., any temp.	Aluminum Sulphate	Fluosilicates
Hydrobromic, any conc.	Ammonia	Fluorine Compounds
Lactic, any conc.	Ammonium Sulphate	
Oxalic, any conc.	Aniline Salts	
Phosphoric, any conc.	Benzine Soaps	
Sulphuric, up to 50%	Calcium Chloride	
Sulphurous	Calcium Hypochlorite	
Tannic	Carbonated Waters	
Tartaric	Chlorine	
BASES	Chlorine Water, Saturated	
Ammonia	Chloride of Lime, Solutions	"HAVEG" IS NOT RESISTANT TO
Caustic Lime	Copper Sulphate	
Neutral Soap Solutions	Ferric Chloride	
Phosphates	Ferrous Chloride	Acetone
Potassium Carbonate	Ferrous Amm. Citrate	Chromic Acid in Higher Concentrations
Sodium Carbonate	Hydrogen Peroxide	Nitric Acid
Sodium Sulphide (Alk. Free)	Hydrogen Sulphide	Organic Bases, as Pyridine
SOLVENTS	Magnesium Chloride	Potassium Hydroxide
Alcohol	Manganese Sulphate	Sodium Hydroxide
Carbon Tetrachloride	Milk of Lime	Sodium Hypochlorite
Ethylene Chlorhydrin	Oxalates	Sulphuric Acid, hot Concentrated
Hydrocarbons	Paraffin	
Oils	Potassium Iodide	
Petroleum	Sulphur, molten	
Trichlorethylene	Sulphur Monochloride	
	Sodium Peroxide Solutions	
	Water Glass	
	Zinc Chloride	

FIG. 2. Table of Resistance of Haveg to various chemicals.

has been developed, of distinctly improved chemical resistivity, from which large and complicated chemical equipment can be produced at costs entirely within reason. This was developed in Germany about ten years ago by the Säureschdutz Gesellschaft M.B.H., and is known under the trade name of "Haveg." [6, 8]

The improved chemical resistivity of Haveg is due in great part to

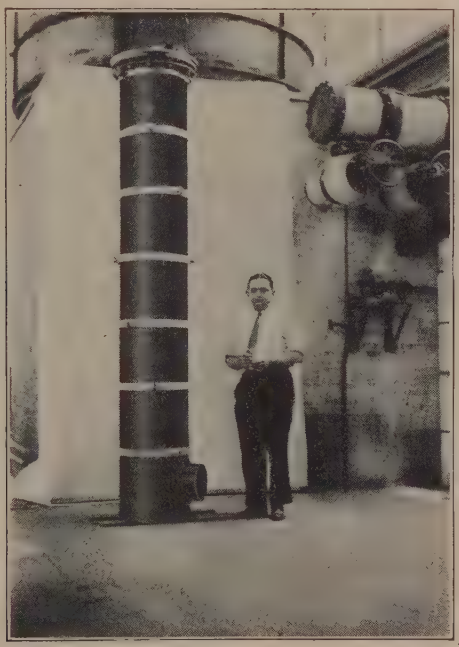

FIG. 3. Haveg washing tower 18" diameter, 10 ft. high, with removable top and integrally molded outlets. Steel bands are used to aid in withstanding pressure.

the fact that instead of cellulose as a filler, a special type of treated asbestos is used, which is itself quite resistant to acids. In conjunction with this asbestos is used a phenolic resin of a distinctly unconventional type, and superior to most conventional resins in toughness and imperviousness to moisture. Penetration of acid into the mass is therefore greatly reduced, and will not cause disintegration in any case, since the filler is not subject to attack. In addition to the chemi-

cal resistivity, the fibrous asbestos, interlaced in the molded mass, gives Haveg a considerable degree of strength and shock resistance.

Large and complicated pieces are made economically feasible by the fact that the Haveg process permits the reduction of molds and mold charges to a minimum. As with conventional materials, the molding of Haveg involves the use of heat and pressure, but the molds

FIG. 4. Cylindrical tank of Haveg, about 1000 gals. capacity, with dished head, liquid level window, and plug outlet in bottom operated by lever mechanism. Note bands used as exterior support. Note also manner of holding on head, with split steel angle ring in a slot, bolted to a flat steel ring placed over the head.

required differ from conventional types in that a relatively flimsy construction is permissible. Molds can, in fact, be made from nearly any constructional material, including wood, metal and even cloth, and this naturally results in greatly lessened production costs, especially where only one or two pieces are required of a given type.

This feature makes it possible, for instance, to mold a single piece tank 9 ft. in diameter and 9 ft. high, in which the total mold and tooling charge is in the vicinity of thirty dollars. The possibility of

molding large pieces of equipment at nominal cost has resulted, in the space of a few years, in the production of a large number of very diverse types of Haveg apparatus for the European and American chemical and textile industries. Among these types may be listed cylindrical and rectangular tanks, scrubbing, reaction and fractionating towers, filter press plates and frames, crystallizing pots, drying trays, agitators, buckets and dippers, fans and ventilators, fume ducts, pipe, valves and fittings, pumps, drip pan systems, separators, precipi-

FIG. 5. Battery of 9 ft. diameter Haveg tanks of about 4000 gallons capacity each. Note use of wooden staves and steel bands as exterior mechanical reinforcement.

tators, vacuum filters, shipping containers, dyeing machines and other textile equipment, and many others.

The chemical engineer responsible for the selection of chemical equipment should have a good understanding of the basic fundamentals of Haveg design, of its major utility, and of its physical and chemical limitations.

The essential consideration in regard to design of Haveg equipment is the fact that Haveg is a molded plastic, not a metal. Apparatus should, therefore, be as simple as its intended use will permit. While the Haveg process permits their inclusion where necessary, undercuts, hollow sections and sharp internal corners should be avoided, as they increase expense. Wherever sharp directional

changes must be included, as in joining tank walls to the bottom, a fillet should be provided. Both very thin sections (below ¼") and very thick sections (above 2") cause difficulty in molding, and should not be employed.

The strength of Haveg (tensile, 2500 lbs. per sq. in., transverse 5500 lbs. per sq. in., compressive 10,500 lbs. per sq. in.) is entirely adequate for self-supporting apparatus even in large sizes, but it follows that heavier wall thickness should be used than with a metal,

FIG. 6. Rectangular Haveg digestion tank 7 ft. square, 4 ft. deep. External steel ribs are used to add strength and to protect from injury.

up to about 1¼", for example, on a 9' × 9' tank. Where abusive mechanical conditions exist, in large equipment, and where it is desired to use the minimum thickness, external re-enforcement should be provided. On cylindrical tanks this takes the form of metal bands (Figs. 3 and 4) or a combination of wooden staves and metal bands (Fig. 5). In cases of heavy internal pressure the Haveg tank can be completely enclosed in a steel shell. On rectangular tanks the re-enforcement consists of a steel rib structure (Fig. 6). In the case of agitators the re-enforcement is internal, consisting of a rigid metal core. (Fig. 7.)

The size of individual units of Haveg equipment is limited by existing equipment to about 12 ft. high with an 18" diameter or about

9 ft. with a 9 ft. diameter. This does not limit the size of finished equipment, however, as individual sections can be joined together to form tall towers, long rectangular pickling tanks, pipe lines, etc. This is accomplished in the case of towers (Fig. 8) by placing a split angle ring in a slot on either side of the joint, and bolting together on a gasket. Pipe lines are joined by a split ring placed in a slot in the Haveg, and followed up by a solid flange (Fig. 9). In this general manner equipment can be produced of considerable length, heads can be fastened on tanks (Figs. 3 and 4) and many other modifications can be accomplished.

Fig. 7. Three bladed Haveg agitator about 6 ft. in diameter, molded over a steel core to add strength and rigidity.

It should be emphasized that Haveg is not a plaster or dope which can be applied as a coating or lining to existing equipment. It is, on the contrary, a solid constructional material. The acid resistance is therefore the same throughout the entire mass. This opens up the possibility of repairs to or alterations on existing Haveg apparatus, as the new surfaces thus exposed are just as resistant as the old.

Among the physical limitations of Haveg should be mentioned the fact that being a plastic, it cannot normally be held to close dimensional tolerances. It has a low coefficient of heat transfer, which while an advantage as far as heat losses are concerned, precludes its use in heating coils or steam jackets. Haveg is unaffected even by

rapid temperature changes, due to its low coefficient of expansion, but it is not recommended for use at temperatures above 135° C. because there is a continued polymerization of the resin beyond this point which tends to form gas and blisters.

In regard to the chemical utility and limitations of Haveg, there is fortunately a groundwork of European experience from which fairly definite recommendations can usually be made[6, 7]. Fig. 2 shows a table of chemical resistance for Haveg, based on this experience. It will be noted that Haveg is resistant to most inorganic and

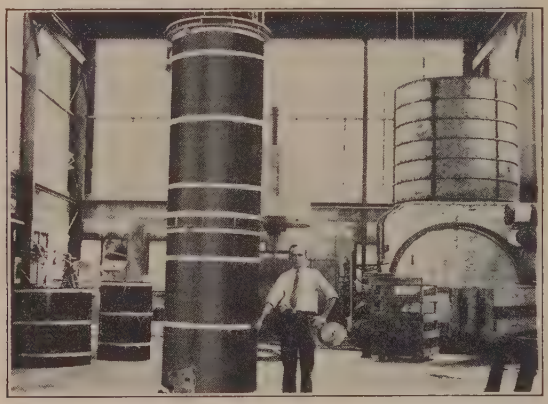

FIG. 8. Haveg tower 36″ diameter, 14 ft. high, made in two sections. Joint is made by means of two split angle rings set in slots and bolted together.

organic acids (including hydrochloric even at boiling temperature) to many solvents and salts, to certain of the weaker bases, and to a number of other chemicals, including chlorine, but not bromine or iodine. The strong oxidizing acids such as nitric, chromic and concentrated sulphuric, attack the organic resin bond in Haveg, as do also the strong caustics like sodium hydroxide, strong resin solvents like acetone, and the organic bases of the aniline series.

Hydrofluoric acid and the fluorine compounds would naturally attack the asbestos filler used in ordinary Haveg, but a special grade is available which contains a carbonaceous filler and which is therefore resistant to these compounds. This grade is also equally resistant to the normal grade against other substances, but it is inferior to it in physical strength, and therefore not so generally applicable.

There are many cases where definite recommendations based on past experience cannot be given. While predictions of Haveg service can frequently be made by analogy in these cases, it is always safer to try samples with the chemicals in question. In this connection, the writer has found laboratory tests not always conclusive, and believes it is better to make such tests under actual plant conditions by suspending the sample as near as possible to the location where the Haveg will be used.

There is still another modification of the phenolic resin plastics which has recently found considerable application in the chemical industry. This is a cold-setting acid proof cement, known in the trade as "Havegit." It consists of a putty-like combination of fillers with

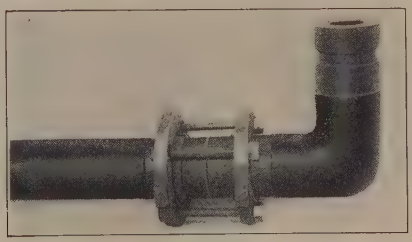

FIG. 9. Manner of joining Haveg pipe. Small split rings are set in slots near the end and a solid flange backs them up, preventing them from dropping out and assuring a good bearing. A gasket is used between the sections.

a phenolic resin which upon the addition of an alcoholic solution of sulphuric acid hardens within a few hours' time to an insoluble, infusible state not unlike that obtained with heat and pressure. The chemical resistance is just about the same as with Haveg.

The major utility of this cement is in the setting up of tile or brick linings in tanks, towers, reactors, etc. It has also been used to cement in place Haveg sheets as a lining in pieces too large to be made of solid Haveg units. In both cases a double or triple layer construction is recommended, with staggered joints to avoid pinholes or other imperfections in installation. Havegit is not usually satisfactory when used alone as a coating, because of the adverse effect of expansion differences between it and the existing apparatus.

The considerations which govern the selection of the proper type

of phenolic plastic for a given job, are both economic and chemical. Where conditions of concentration and temperature are not severe the use of laminated or molded grades in pipe lines or other small simple shapes will result in considerable economies. With more rigorous conditions of corrosion and with larger equipment, the use of Haveg is indicated, and finally, with apparatus too large to be constructed economically from Haveg, the use of Havegit cement in tile or Haveg-plate linings will usually be more satisfactory.

It should be pointed out in conclusion that in addition to the severe cases where the utility of these materials is more or less obvious, there are other more moderate cases where fairly satisfactory operation is now possible, yet where the phenolic plastics can show advantages. In such cases the consideration is largely economic and the decision rests on the relative costs and life expectancies of the respective materials.

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Discussion

Chairman Marshall: Thank you, Mr. Adams. We have a few moments for the discussion of Mr. Adams' paper. If there are no questions we will proceed to the next paper on the session's program—"The Trend of Chemical Utilization in Petroleum Refining," by Mr. P. C. Keith, Jr., and Mr. H. O. Forrest, of the M. W. Kellogg Company, New York City. Mr. Keith will present the paper.

THE TREND OF CHEMICAL UTILIZATION IN PETROLEUM REFINING

By P. C. KEITH, Jr.,* and H. O. FORREST *

A detailed and comprehensive discussion of the chemicals used in the production of each individual product of the petroleum industry is obviously outside the scope of this paper. The products are too numerous and the methods of treatment vary considerably in detail. However, the three products of major importance requiring well over 90% of all chemicals are gasoline, kerosene, and lubricating oil, and the general trend of chemical utilization is defined by them. For this reason most of the discussion in this paper will be limited to the chemical treatment of these products as practiced in 1920 and as developed up to the present time.

In the early days of petroleum refining sulphuric acid and caustic soda were the primary treating agents in the industry. Acid was used to remove sulphur, malodorous and bad colored compounds, while caustic was used for neutralization, and, when mixed with lead oxide to form "doctor" solution, to sweeten lighter hydrocarbons. While such treatment reduced the yield, it resulted in a gasoline having a more desirable odor and color, a kerosene with more satisfactory burning qualities and, in the case of lubricating oils from inferior crudes, a product more nearly approaching Pennsylvania quality than that of the raw stock.

Since good color and odor were the primary requisites, the objectionable materials which were removed were considered as waste and the only thought regarding them was to devise a satisfactory means for their disposal. The economic situation did not demand that any real attention be given to the possibility of loss of valuable products due to overtreatment. However, during the past fifteen years the various oil companies and affiliated industries have organized technical and scientific development on a large scale. This factor, together with the increased pressure of economic conditions, has introduced new chemicals and treating methods, with the result that

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the percentage of crude thrown away as sludge waste is much less than formerly, despite the more rigid specifications of the finished products. Whereas the only chemicals of importance were acids and alkali, they now range from these basic materials through special refining solvents to chemical addition agents which are used to modify the properties of the otherwise finished oils.

The diagram, Fig. 1, indicates very generally the important steps in oil refining which used chemicals prior to 1920. The use of sul-

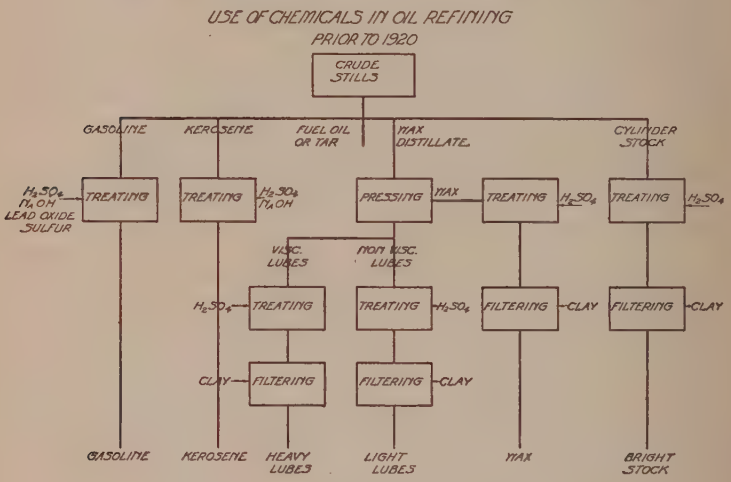

Fig. 1

phuric acid with the treating methods then employed to remove the undesirable sulphur and unsaturated compounds, which accounted for the oil's bad color and odor, usually resulted in large losses. To make a satisfactory bright stock or a cylinder stock from Mid-Continent oils it was customary to use from 40 to 60 pounds of acid per barrel, each pound of acid causing approximately 1% loss. Even with this loss the paraffinity of the final product did not equal that of Pennsylvania oil. As late as 1925 the cracked gasolines from some high sulphur crudes were treated with as much as 40 pounds of concentrated sulphuric acid per barrel. Such a treatment frequently resulted in as much as 50% of the cracked distillate being discarded in the form of acid sludge. From some crudes it was impossible to produce a satisfactory kerosene.

These losses and changed economic conditions caused the industry to seek improved treating methods. The pertinent figures relating to the use of sulphuric acid in the petroleum industry are shown in

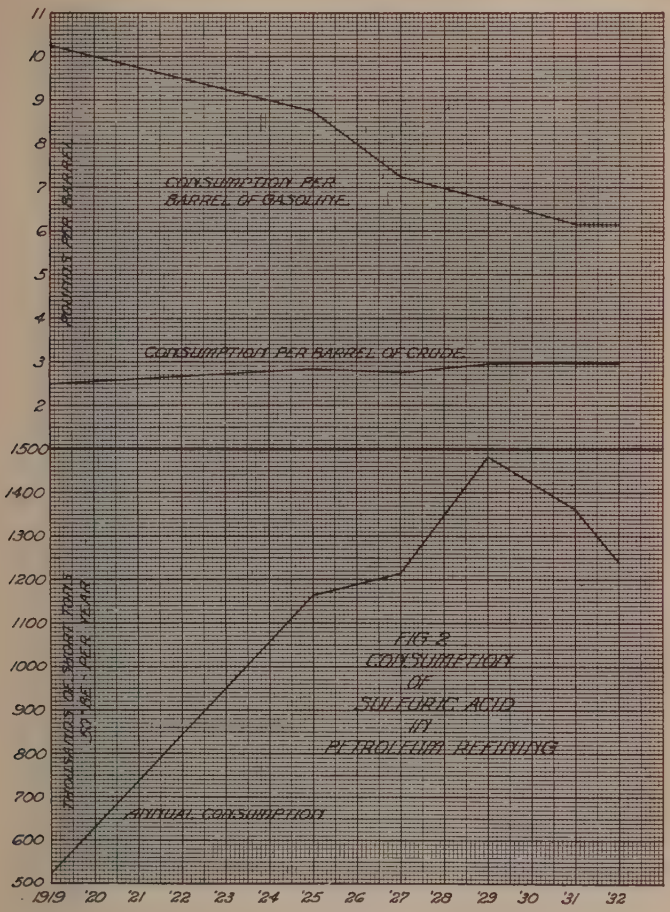

FIG. 2

Fig. 2. The total consumption increased from 522,060 tons of 50° Be acid in 1919, to 1,483,863 tons in 1929 and then decreased to 1,240,000 tons in 1932. While the amount used per barrel of crude

has changed only slightly during this period, the improved treating methods are reflected in the decreased consumption per barrel of gasoline. These figures do not reveal the extent of the improvement, since no allowance has been made for the increased percentage of cracked gasoline and of gasolines having a higher initial sulphur content. If proper allowance could be made for these two factors, the effect of improved treating methods would appear even more marked.

The major improvement was the substitution of continuous counter-current treatment for the batch process. Various modifications of the continuous process have been made to control, (1) acid treating strength by sludge oil recirculation (Gary),[1] (2) contact time by the use of centrifuges (Cross,[2] Stratford[3]), and (3) temperature of treatment by refrigeration (Halloran[4]). The net effect was an increase in the selectivity of the acid which reduced not only consumption but also sludge loss.

The total amount of caustic (sodium hydroxide and soda ash) used should be independent of acid consumption since only the acid remaining after settling need be neutralized. Fig. 3 shows that the amount per barrel did remain reasonably constant until 1929. Thereafter there has been a definite reduction. Prior to 1929 there were improvements in caustic utilization of the same type as have been mentioned for acid and it is the author's opinion that a decrease in the amount used per barrel would have been registered had it not been for the large production of high sulphur-bearing West Texas crude and the increasing tendency to combat corrosion with caustic. Since 1929 the gradual decline of the West Texas fields, the increasing use of "contact" clay for lube oil neutralization, and the improvement in treating methods, particularly the recovering of spent "doctor" solution, explain the declining consumption.

"Doctor" solution is a mixture of litharge and sodium hydroxide and is used to "sweeten" the lighter hydrocarbons. Prior to 1929 it was common practice to discard the spent solution. In 1929 the oil industry began to install recovery plants, in which the "spent" doctor was air-blown to oxidize the lead sulphide to lead oxide. Additional small amounts of lead oxide and caustic are added to keep the solution at full strength. The litharge figures shown in Table I shows the reduction in use from 1929 to 1932.

TABLE I. LITHARGE CONSUMPTION IN PETROLEUM REFINING

Year	Short Tons
1929	13,615
1930	12,028
1931	7,331
1932	4,793

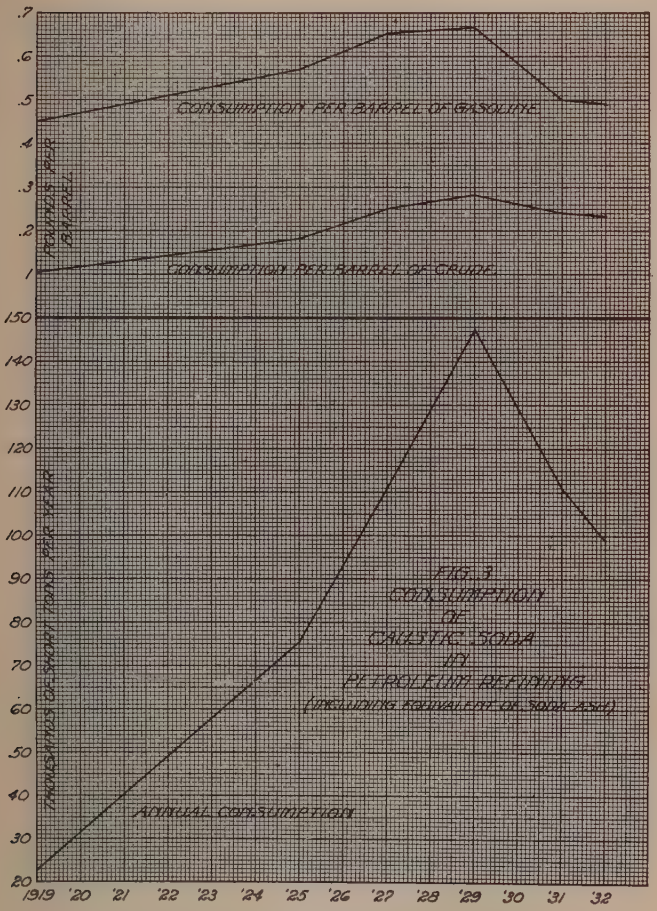

FIG. 3

Calcium-hypochlorite is successfully used as a substitute for "doctor" in sweetening. No production figures for this chemical are

available, but since its widest application is found in the natural gasoline industry, it is probable that its production has declined with natural gasoline production.

As has already been mentioned, the use of acid and caustic imposed quality limitations, which the oil industry was anxious to avoid. Probably the first step in removing these limitations was the introduction of the Edeleanu SO_2 process.[5] From some California crudes it was impossible to produce with acid a kerosene possessing satisfactory properties. In 1925 the first American Edeleanu plant was installed. Being much more selective than acid, a better product was produced, and removal of undesirable constituents taking place essentially by physical solution rather than by drastic chemical reaction, the deterioration of oil to acid sludge was minimized. The Edeleanu process is the fore-runner of the more selective and less destructive solvents to which the industry is now rapidly turning. At the present day thirty-five Edeleanu plants have been installed throughout the world, with a total treating capacity of 78,000 barrels per day of light oil and 13,000 barrels per day of lubricating oils. Ten of these plants, with a total capacity of 36,000 barrels per day, are in America.

The increased use of chemicals in the petroleum industry is indicated by the diagram of Fig. 4, which shows the application of various reagents in present practice. As in the earlier methods of Fig. 1, sulphuric acid is still the predominant treating agent, but other materials have assumed important places in the complete scheme of operation. So greatly is this the case that in one refinery, operating on a relatively low grade crude, the cost of acid was only 20% of the total cost of chemicals used, although it was over 85% of the total quantity of reagents used. The total cost of basic chemicals, including acid, alkali, litharge and sulphur, was only 40% of the total, the more expensive chemicals in small quantities being responsible for the remaining costs.

Gasoline treating has always been the major use of sulphuric acid in the petroleum industry. As pointed out previously, it was essential in the early days to provide a finished product of satisfactory color and odor, irrespective of the losses entailed. The action of sulphuric acid is not one of real selectivity and it became increasingly evident that serious losses of valuable constituents were taking place by polymerization and solution in the sludge. With the development of cracking on a broad scale, and the consequent increase of the

unsaturated constituents in the gasoline, the reduction of this loss became an item of major importance, merely from a yield standpoint. In addition, in 1926 the anti-knock characteristic of a motor fuel began to be of increasing importance. Higher temperature cracking to produce higher anti-knock gasoline resulted in untreated products having a large proportion of unsaturated compounds. Conventional methods of treating resulted not only in lower yields but in marked reduction in anti-knock value and it became imperative to decrease treating losses. The improvements in acid treating have already been

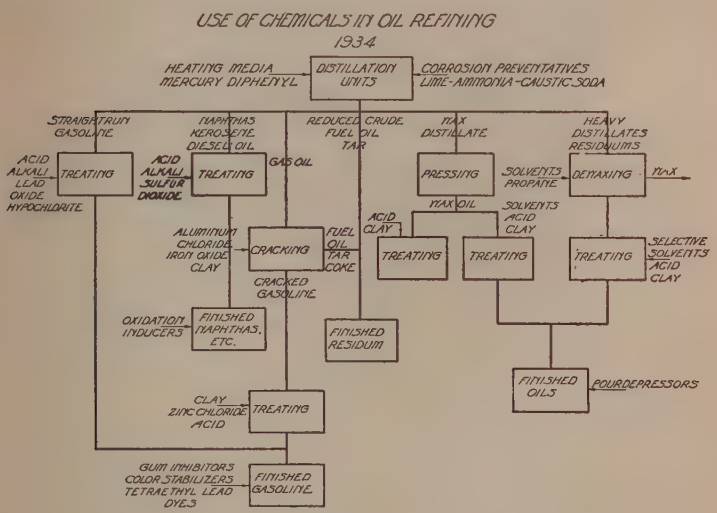

Fig. 4

mentioned. But however acid is used, it results in a loss of yield and of anti-knock value.

The substitution of clay treating of the cracked gasoline, particularly in the vapor phase, as in the Gray process, has been an important factor in reducing the consumption of treating chemicals and in retaining the desirable materials in the finished product. Unfortunately, while decreasing gum content and increasing color stability, the clay process does not remove sulphur and consequently large quantities of cracked gasoline are still acid treated. Following clay treatment the gasoline must be sweetened, but the marked loss of yield and anti-knock value is avoided. However, if the 100,000

barrels per day of cracked gasoline now clay refined were treated with acid the consumption would be an appreciable portion of the total acid used. Competitive with the Gray process is the Lachman process [6] which treats gasoline vapor with zinc chloride. The loss of zinc chloride is extremely small, the chemical apparently acting as a catalyst.

These new developments in the refining of gasoline may be considered as color and gum removing processes directly, rather than as processes for removal of unsaturated hydrocarbons. They are indicative of the general trend toward greater selectivity in the action of chemicals. The aim is to remove only those constituents which are a definite disadvantage in the finished product and to do so with the least possible effect on the desirable products.

The trend is even more marked than is indicated. Instead of treating to a satisfactory gum content, the tendency is to proceed only part way and add inhibitors of gum formation. The Government's ruling that gasoline containing tetra-ethyl lead had to be dyed a distinctive color opened the way for colored gasolines. Because of the increasing percentage of cracked gasoline the refiner found it more and more difficult to produce a color stable product. Since color, as such, has no effect on motor performance and the achievement of a color stable product by refining methods is more expensive than by adding dyes, almost all gasoline at the present time is colored. These expedients have resulted in a greater yield of a product which is fully as satisfactory.

One of the greatest developments, from a chemical viewpoint, is the use of tetra-ethyl lead to reduce the tendency to detonate. Although no figures are available on the use of this material, it probably represents the major chemical cost to most refiners. Its expanding use has greatly increased the total cost of chemicals, but has resulted in an improvement of the product without a consequent reduction in yield.

The treatment of gasoline to produce a satisfactory and salable product has therefore changed from a drastic chemical reaction with large losses to one in which the treatment is more selective and is carried only far enough to produce a satisfactory and stable product with chemical additions compounds insuring satisfactory color, gum, and performance characteristics.

What has taken place in gasoline refining technique is taking place in the technique of lubricating oil manufacture. The period

from 1920 to 1932 saw an enhanced production of lubricants by vacuum distillation. This procedure eliminated a large part of the acid required for treating. Acid consumption was further reduced by removing more color units by contact filtration. Incidentally caustic consumption decreased since the clay satisfactorily neutralized the remaining acid. During part of this period some refiners were able to select stocks for the production of lubricating oil which required a minimum of treating to bring them to satisfactory specifications. However, an offsetting influence, increasing the use of acid, was the trend toward lighter colored lubricating oils.

Forced partly by competition, but also by improved motor design and the increased use of cars, there has been a marked tendency to stress characteristics of lubricating oils which were not considered ten years ago. Among these the most important from the viewpoint of the chemical industry are viscosity index, resistance to sludging and oxidation, and pour test. Viscosity index may be considered as an empirical method of expressing the reciprocal of the slope of the temperature viscosity curve, with Pennsylvania oils having a value of about 100 and Coastal oils a value of about zero. Pour test is a measure of the minimum temperature at which an oil will flow and in most motor oils is a function of wax content. It is the opinion of most refiners that they will be forced to manufacture motor oils having a viscosity index of 100 and a pour point of 0°F., if for no other than sales reasons.

In general, the widely used present-day methods will not treat and dewax sufficiently well to fulfill these requirements. This fact is of importance to the chemical industry since the oil industry may look to it to supply dewaxing and treating solvents. While the production of lubricating oil may not increase, it is probable that the amount of oil to be dewaxed to produce the same quantity of lubricants will increase. This is true because those crudes having a low wax content also generally have low contents of high viscosity index oil. It is also probable that the crude run to lubes will increase because the yield of a 100 V.I. oil will be less than the present lube yield. This lower yield is caused not by the deterioration of the crude by the treating methods contemplated but by the radical improvement of the motor oil. From most crudes this improvement is not economically possible by acid technique. The undesirable constituents removed by a selective solvent are utilizable as fuel oil or cracking stock, whereas acid sludge presents a disposal problem.

The processes which have been developed for improving these two characteristics of lubricating oil, although essentially physical in operation, require large quantities of chemicals which are relatively new to the petroleum refining industry. The new processes developed for dewaxing are:

1. Benzol-acetone process.[7]
2. Chlorinated solvents process.[8]
3. Propane process.[9]

It is not the purpose of this discussion to compare the relative merits of the various processes, but merely to indicate the effect of their development on chemical utilization. During 1929 the lubricating oil production as shown in Table II was approximately 34,000,000 barrels, or nearly 100,000 barrels per day. Although the production has decreased somewhat since that time, it may be safely assumed that it will return to at least this value in the near future. This is particularly true in view of the increased tendency for motor manufacturers to recommend lower viscosity oils, with a consequent increase in consumption.

TABLE II. PETROLEUM STATISTICS

(A.P.I. Statistical Bulletin, 1933)

Year	Crude Consumption Barrels	Gasoline Barrels (42s)	Lubricating Oils Barrels (42s)
1919	422,740,000	99,648,000	20,161,000
1920	521,876,000	122,259,000	24,438,000
1921	520,044,000	130,900,000	20,896,000
1922	584,547,000	150,054,000	23,304,000
1923	715,980,000	192,650,000	26,168,000
1924	752,458,000	228,650,000	27,498,000
1925	828,885,000	266,810,000	31,055,000
1926	842,082,000	304,493,000	32,293,000
1927	879,037,000	337,348,000	37,721,000
1928	950,066,000	384,913,000	34,658,000
1929	1,024,039,000	441,804,000	34,359,000
1930	952,998,000	441,702,000	34,201,000
1931	913,759,000	440,011,000	26,704,000
1932	831,341,000	402,063,000	22,433,000

In the practical operation of these processes, it is inevitable that some of the chemical be lost, and it has been indicated that the magnitude will be about one-tenth of one percent of the amount circulated. On the assumption that 10,000 barrels per day, or ten percent of the 1929 production, may be allocated to each of the three

processes, it is possible to arrive at a quantity of each of the solvents which may be required. Obviously, a definite prediction of the amount of each material is impossible without an accurate analysis of each process and some gift of prophecy, and the prediction would vary according to personal convictions.

The total quantity of lubricating oil fractions charged to the dewaxing process will be much greater than the final production. For example, if a wax-bearing California residuum such as Kettleman Hills is to be processed, with approximately 25% removal of the asphalt by distillation, or by propane deasphalting, 10% removal on dewaxing and 35% removal on solvent treating, all based on the original residuum, the net charge to the dewaxing plant will be 250 percent of the finished oil if dewaxing occurs prior to treating and 133 percent if dewaxing follows treating. In the case of a Mid-Continent oil the corresponding figures would be about 200% and 125% respectively. A reasonable estimate of the charge to dewaxing plants in each process is, therefore, about 18,000 barrels per day.

The average composition of the solution being dewaxed will be approximately 25 percent oil and 75 percent solvent. The solvent circulated per day would then be 54,000 barrels and a reasonable quantity for initial operation would be about one-half of this quantity, or 27,000 barrels. The loss at one-tenth of one percent would be 54 barrels per day, or nearly 20,000 barrels per year. If this capacity is to be installed over a three year period the solvent requirements during the first three years would be 12,300, 19,000,and 25,700 barrels per year and subsequent to that time would be 20,000 barrels per year.

In the use of the acetone-benzol process the average composition of the solvent will probably be about 65 percent benzol and 35 percent acetone, although present developments indicate the possibility of using 52% benzol and 13% toluol. On the latter basis the approximate quantities of benzol, toluol and acetone required would be 440,000, 109,000, and 294,000 gallons per year. The acetone quantity of nearly 2,000,000 pounds per year is a considerable fraction of the actual production of this chemical. The additional demand for this material is an important item to the chemical industry, and is one example of the trend toward higher value chemicals. The demand for benzol would not have an appreciable effect on the supply. The toluene demand could be readily supplied in normal times, but might

be a factor when it was in great demand for the manufacture of explosives.

The demand for propane in the propane dewaxing process [9] is only a very minor fraction of the readily available supply and since it would normally be a product of the petroleum industry, its effect on the chemical industry is of no importance.

The chlorinated solvent processes again require relatively large amounts of higher priced chemicals. The material disclosed as the solvent in this process in Pester's paper [8] was trichlorethylene, and although the Bachlund patent discloses other chlorinated compounds of this type which may be used as the diluent, this material may be considered as typical. Under the previous assumption of 840,000 gallons, or 10,800,000 pounds per year, the demand would require a large increase in present day production capacity.

These developments in dewaxing of lubricating oils have resulted in the introduction to the petroleum industry of at least two new chemicals, trichlorethylene and acetone, and three hydrocarbon solvents, benzol, toluol and propane. The newer developments in solvent treating processes are responsible for many more which will undoubtedly be of increasing importance in the future. The more important of these processes which have been disclosed at the recent meeting of the American Petroleum Institute are:

1. Chlorex Process—using B-B'dichlorethyl ether.[10]
2. Crotonaldehyde Process.[11]
3. Duosol Process—using propane and cresylic acid.[12]
4. Edeleanu Process—using sulphur dioxide or sulphur dioxide and benzol.[13]
5. Furfural Process.[14]
6. Nitrobenzene Process.[15]
7. Phenol Process.[16]

The primary purpose of solvent treating is improvement in the quality of lubricating oil, particularly with regard to viscosity index. At the same time, an improvement in color, Conradson carbon and resistance to oxidation is obtained. A simple concept of the untreated oil is a mixture of three major classes of compounds, asphalt, naphthenes and paraffins. The asphaltic materials can be separated to a major degree by distillation under vacuum, by precipitation from a propane solution of the oil,[17] or by the solvent itself. The latter

methods may be considered as part of the general trend to carry out refining processes by the use of chemicals, in order to permit greater selectivity of separation of desirable from undesirable constituents.

The oil will contain naphthenes and paraffins in varying proportions depending on the crude from which it is produced. For example, in Pennsylvania oils the proportion may be as high as 90 percent paraffins, while in California oils from waxy crudes it may be as low as 50 percent, of which one-half is wax. In non-waxy crudes the paraffin content may be so low that economical recovery is impossible. A desirable solvent treating process is one which selectively separates the undesirable naphthenes from the desirable paraffins, and permits recovery of both without serious impairment. In this respect particularly it differs from the older acid treating process which merely removed the minimum of color bodies as waste products to give a satisfactory color.

All of these processes depend upon selectively absorbing the naphthenes in the solvent and thus separating them from the paraffins. The feasibility of using any particular solvent depends on many factors, including selectivity, or ability to dissolve a maximum of the naphthenes and a minimum of paraffins, cost, availability, ease of recovery, stability and chemical inertness. A very large number of compounds have been investigated [18] and although the seven materials that have been developed may seem extensive, they represent only a small fraction of the possibilities and may be increased as other compounds become more available.

As in the case of dewaxing, it is impossible to determine the possible requirements of these chemicals for the oil refining industry, particularly since the proportion assignable to each of the seven processes depends on so many factors. The total lubricating oil production of 100,000 barrels per day has been estimated as divided into 30 percent from Pennsylvania base, 32 percent from mixed base similar to Mid-Continent, 31 percent from Coastal and 7 percent from California. Because of the inherent composition of the oils, the amount of treatment to reach a given viscosity index varies widely with the source. For example, it is possible to obtain approximately 100 V.I. oil from Pennsylvania crude without solvent treating or with 100% yield based on oil as finished today. In the case of California wax bearing crudes such as Kettleman Hills, however, the yield might be only 35 percent and for Mid-Continent oils only 75 percent of present yields. With non-waxy California or Coastal oils

the yield would be so low as to make their use uneconomical. In view of the probability of some use of solvents even on Pennsylvania oils to increase the viscosity index beyond the value which would be feasible for other oils, it is probably fair to assume an average treating yield of about 70 percent. On this basis the quantity of oils to be treated would be approximately 140,000 to 200,000 barrels per day, depending on whether dewaxing followed or preceded treating. Assuming 10% of the lower figure would be treated by each of the seven processes and three volumes of solvent per volume of oil treated, the actual daily throughput of solvent would be 1,760,000 gallons per day. With the loss at only 0.1%, the replacement would be 640,000 gallons of each of the solvents mentioned.

An indication of the possible effect of the demand for these materials on the chemical industry may be obtained by comparing the above figures of 640,000 gallons per year with the present production and consumption. For the years 1931 and 1932 the only figures available are for cresylic acid and phenol, which are coal tar products. The 640,000 gallons per year is equivalent to about 5,600,000 pounds per year, or more than 50 percent of the cresylic acid production in 1931 and more than 100% of the sales in 1932, as shown in Table III. It is even 45% of the phenol sales in 1932, as reported to the U. S. Tariff Commission.

TABLE III. PRODUCTION AND SALES OF CRESYLIC ACID AND PHENOL

(From U. S. Tariff Commission Report)

	Cresylic Acid	Phenol
1931		
Production, lbs.	10,994,000	17,981,000
Sales, lbs.	10,305,000	14,002,000
1932		
Production, lbs.	8,060,000	13,965,000
Sales, lbs.	4,850,000	12,181,000

Unfortunately, figures are not available for most of the other solvents, and although some of them may be made by relatively simple chemical processes, from cheap raw materials, the majority are in the special chemical classification. One of these, nitrobenzene, is produced in large quantities as an intermediate in dye manufacture and the requirement on the above basis is only about 12% of the 1929 production. However, the use of such quantities of most of these

materials would have a definite effect on the chemical industry. New methods of manufacture in large quantities and new sources of raw materials would undoubtedly have to be developed in many cases to supply this demand.

In the above discussion no mention was made of chemical addition agents which may be added to lubricating oils in much the same manner as addition agents are added to gasoline. At the present time there is a wide-spread use of the pour-depressor Paraflow. This product may be added to a partially dewaxed oil to decrease its pour point from approximately 15° F. to 0° F. Other addition agents, such as some oleates and stearates, are added to enhance the ability of the oil to form and maintain a film over metal surfaces. Still another chemical, when added to a lubricating oil, will markedly increase the viscosity index. More and more of these addition compounds will be used in the future to modify the properties of the finished lubricant.

The previous discussion has presented the development of chemical utilization in the oil industry from a position where basic chemicals were a necessary evil, with the only requirement that of destroying the undesirable fractions, to the present position, where they aid in the production of higher grade products. Originally a minor item of operating cost because of both the generally higher costs of refining and cheap chemicals, they now represent a large part of the cost in many refineries because other operating costs have been greatly decreased and the number and unit price of chemicals has greatly increased. The trend has been definitely from destructive chemicals to more selective and higher cost chemicals in the refining processes, and to the use of chemicals for imparting the final desired characteristics to the products.

This trend may be emphasized still further, from the viewpoint of the chemical industry, as a trend from destructive inorganic chemicals, through less destructive inorganic chemicals to selective and non-destructive organic chemicals and addition agents.

During the early part of this period the trend may be considered as a gradual one, with no marked entrance of the chemical industry into oil refining. The first major development, requiring the refiner to relinquish his essentially self-contained position, was the introduction of tetra-ethyl lead. Its significance in the trend of chemical utilization cannot be emphasized too greatly, because it marked the beginning of the industry's acknowledgment of addition agents. It

may also be considered as the entrance of the organic chemical industry into oil refining and as a stepping-stone toward the present organic chemical consciousness of the petroleum refiner.

Any prophecy of the future trend of chemical utilization in the petroleum industry is of necessity visionary, but it may be safely stated that it will continue to be toward more complex and selective materials, and that high yield of high quality products will be more and more important as the supply of high quality crudes decreases. Addition agents for increasing the apparent viscosity index and sludging characteristics of lubricating oils and competitive anti-knock compounds for gasoline are probable developments. Catalytic cracking and the addition of some chemical during the cracking operation to produce high anti-knock compounds directly in the gasoline are distinct possibilities for the future. Certainly the selective treatment of lubricating oils, and possibly of other fractions, is still in the preliminary stages from a chemical viewpoint, and considerable further development along these lines may be anticipated.

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Discussion

Chairman Marshall: We have some time available to question Mr. Keith or to discuss his paper. We have some of our friends from the oil industry here and some who are engaged in the manufacture of sulphuric acid.

A. M. Fairlie (written): The statement is made and repeated at least twice in the paper, that the loss of chemicals is only one-tenth of one per cent of the amount circulated. The figure given for the chemical loss is a remarkably low one, and I should like to ask whether it has been verified, or is it open to question? It would also be remarkable if the loss of each of the various chemicals used in refining petroleum would be the same, and I am wondering whether more accurate figures cannot be cited, to show the actual loss of chemicals, for each of the various chemicals employed, separately.

Also repeating and amplifying my previous question, I should like to ask the authors whether they can supply any figures (a) as to the amount of sulfuric acid likely to be consumed annually in the production of the new chemicals used to replace sulfuric acid in the refining of pertoleum, assuming all of the sulfuric acid so replaced; and (b) the amount of sulfuric acid required annually to produce the chemical addition agents mentioned on page 343.

P. C. Keith, Jr. (written in reply to Mr. Fairlie): In connection with your question regarding solvent loss of 0.1% you will note that in both cases where this was mentioned it was with relation to solvent requirements. It was not the purpose to give solvent loss figures but merely to show what chemicals would be required with the loss at some low value. The context of the paper clearly indicates that the solvent requirements would be as shown *if* the loss was 0.1% and it is then easy to calculate what the requirements would be for any other solvent loss.

In the paper by Bahlke et al on the Chlorex Process (reference 10) the loss is given as 0.1103 to 0.2571 in Table 6. In the paper by

Ferris et al (reference 15) they used 0.1 and 0.2 for economic comparisons and estimated a value of 0.08%. Manley et al (reference 14) used 0.2% and stated that it was estimated the loss would be reduced considerably below this value. Stratford et al (reference 16) shows 0.15% over a three-year period and indicated a much lower loss at present.

As you undoubtedly realize, it was the purpose of the paper to discuss the trends of chemical use rather than the merits of any one process, and to be conservative in predicting solvent requirements the lower figure of 0.1 was used.

Unfortunately it is not possible to predict the sulphuric acid requirements for the manufacture of the various solvents and addition agents. The methods of manufacture and, in some cases, the chemical composition of materials are not published or readily available. Even if they were, it would still be impossible to predict what changes might become economically advisable in these methods.

R. T. Haslam: I have nothing particularly to add to the discussion, but want to congratulate Mr. Keith on the fine presentation he gave. There is only one objection I have and that was his calling certain things "dopes." Not that it is not true, but it has a bad sound. Seriously, the oil industry in the last ten years particularly, has become much more of a chemical industry in many cases than the chemical industry itself. There is no question but that most of the forecasts Mr. Keith made will come true. There will be found those various chemicals, and when they are found they will be used in huge quantities. I recall when Midgley was working on an anti-knock compound. Every time he found one that had a little anti-knock property he had to worry as to whether there was enough of that compound available. If there was not, he usually stopped working on it. Even a thousandth of one per cent of a compound used in gasoline, builds up a large production almost immediately.

M. Y. Seaton: Mr. Keith, several of the smaller refineries on the West Coast have been substituting for sodium hydroxide magnesium hydroxide for neutralization, and also as a sweetening agent. Can you comment on that particular phase in the use of chemicals?

P. C. Keith: Unfortunately I cannot. I know some are using magnesium hydroxide, but how it is used, the amount used, and the comparative costs I am unacquainted with.

Chairman Marshall: If there are no further questions the next paper is "Prospects of a Petroleum Chemical Industry," by Dr. Carleton Ellis. This links in very directly with the paper by Mr. Keith and Mr. Forrest, and also with this afternoon's visit to the hydrogenation plant of the Standard Oil Company.

There are no preprints available and in explanation of that I might say that our fellow member, Mr. Ellis, came to the rescue of the

Paper Committee when several authors who had made promises found it impossible to devote the necessary time to the preparation of a paper. Mr. Ellis has done a very excellent piece of work in a very short space of time.

THE PROSPECTS OF A PETROLEUM CHEMICAL INDUSTRY

By CARLETON ELLIS

It is not the purpose of my talk to enumerate all the chemical possibilities through the conversion of petroleum material, since the number of these proposals is legion. This I have found in recently concluding the text of a book on "The Chemistry of Petroleum Derivatives," which is now assembled in type and covers nearly twelve hundred pages closely printed of items condensed as much as possible, yet leaves the subject still capable of much expansion.

The publication, however, will make clear to most of us that the real developments involving various chemical engineering problems have fallen to the gases from petroleum rather than to the liquid and high-boiling constituents. One reason for this is that the gases afford us the means of extracting concentrates or even pure hydrocarbons such as methane, ethane, propane, butane, ethylene, propylene, butylene, etc., and therefore we have such concentrates to work upon rather than upon higher hydrocarbons of tremendous complexity, or rather of mixtures which are extremely complex.

Crude petroleum consists essentially of a mixture of hydrocarbons of varying degrees of molecular complexity. In addition there are present smaller proportions of compounds of oxygen, nitrogen, and sulphur together with mechanically held gas, water or clay and inorganic substances either in solution or colloidal suspension. The molecular complexity of the hydrocarbons may range from the simplest members of the paraffin series to hydrocarbons whose molecular weights exceed 1000, and include not only paraffins and cycloparaffins (naphthenes) but also aromatics and polynuclear aromatics and cycloparaffins. The presence of unsaturated hydrocarbons, prior to distillation, has been the subject of much controversy. If such hydrocarbons are in crude petroleum, the proportion must be exceedingly small.

It has been calculated that a hydrocarbon represented by the comparatively low number of 20 carbon atoms would have 366,319 pos-

sible isomers (or 3,395,964, if stereoisomers are considered).[1] The difficulties involved in separating such a complex mixture as petroleum are thus very great. Although many individual hydrocarbons have been isolated by laborious fractional distillation and crystallization methods from petroleum fractions, particularly natural-gas gasoline and both straight-run and cracked gasolines, the gaseous hydrocarbons are more readily separated into their constituents. Also, the gaseous hydrocarbons are generally more reactive. At the present time, therefore, these latter hydrocarbons are the more promising materials for the basis of a petroleum chemical industry.

The first real chemical industry founded on petroleum is, I believe, that in which I had a hand in establishing many years ago, through Standard Oil Company of New Jersey, on the production of alcohols by reaction of the olefins of cracking gas with sulphuric acid.

Cracking Gas

Industrial cracking processes are for the most part concerned with the conversion of high-boiling distillates into low-boiling liquids of the gasoline type. The utilization of the large quantity of lower hydrocarbon by-products (cracking gas) from this procedure is already exerting a tremendous influence on the development of industrial organic syntheses. It has been estimated that the volume of this gas is of the order of 250,000,000,000 cubic feet annually.[2]

The composition of cracking gas is dependent chiefly upon the temperature of cracking. The so-called liquid-phase operations, those employing temperatures below 500° C. and pressures up to 1000 pounds, yield a gas containing a fairly large proportion of paraffin hydrocarbons and relatively small amounts of olefins. Of the latter, propylene is apparently the predominating unsaturated hydrocarbon. Vapor-phase processes, those operating at higher temperatures and atmospheric or reduced pressure, give a cracking gas having a large proportion of ethylene in addition to propylene and other olefins. Diolefins, particularly butadiene, are also present in appreciable quantities (1 per cent or more).

Prior to its utilization cracking gas may be subjected to compression and absorption operations, thereby dividing it into at least two main fractions: (a) gaseous olefins, consisting of ethylene, propylene, and the butylenes, and (b) liquid olefins, consisting of amylenes,

hexylenes, and higher olefins. Further fractionation of these two main fractions is, of course, possible.

Gaseous and low-boiling hydrocarbons may also be obtained from cracked distillates. For example, cracked naphtha, containing the fixed gases soluble in this naphtha at the temperature and pressure of the condensing equipment on the cracking coils, is fed to a tower which is called a debutanizer. About 30 per cent of the most volatile components are taken overhead in this tower and substantially all are condensed. This volatile overhead cut is then fed to a second tower which is called a stabilizer. Here a sharp cut is made between propane and lighter hydrocarbons and butane and less volatile hydrocarbons.[3]

The analysis of the overhead gas is approximately as follows:

Methane and fixed gas	8%	by volume
Ethylene	4%	
Ethane	21%	
Propylene	16%	
Propane	49%	
Isobutane	2%	

The analysis of the bottoms from the stabilizer is approximately:

Isobutane	4%	by weight
Isobutylene	4%	
α-Butylene	3%	
n-Butane	13%	
β-Butylene	6%	
n-Pentane	20%	
Pentylenes	13%	
n-Hexane	15%	
Hexylenes	9%	
Heptane and higher	13%	

With modern pressure-fractionating equipment the separation of liquefied petroleum gases into propane, n-butane and isobutane is feasible. Butane is employed as a carburetting agent and propane, in addition, is used in refrigerating equipment. Liquefied isobutane or propane are extracting agents for the refining of resins and gums [4] or oils and asphalts.[5]

Alcohols

The conversion of olefins to alcohols is accomplished by absorption in sulphuric acid. This method involves the intermediate formation of alkylsulphuric acids followed by hydrolysis. Except in the

case of ethylene, secondary and tertiary alcohols are obtained. The reactions may be represented, for ethylene and propylene, by:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3CH_2SO_4H$$

$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

$$CH_3CH{=}CH_2 + H_2SO_4 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHSO_4H$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHSO_4H + H_2O \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH + H_2SO_4$$

With ethylene and propylene the resulting products are exclusively ethyl and isopropyl alcohols, respectively. With butylenes and higher olefins either secondary and tertiary alcohols, or a mixture, are obtained, as well as a certain amount of polymers.

Possibly the most important factors connected with this method of manufacturing alcohols are the temperature and concentration of the acid, and regulation of these factors determines to a large degree the proportion of olefin converted to alcohol or to polymers. With ethylene, temperatures as high as 60° to 80° C. may be employed [6]; for other olefins (propylene and higher), the temperature is generally kept at 20° to 30° C. or lower.[7] Ethylene is absorbed in 96 to 100 per cent acid, propylene in 90 to 94 per cent acid, higher straight-chain olefins (for example, 1- and 2-butene, 1- and 2-pentene) in 80 to 90 per cent acid, and the iso-olefins (isobutene and isopentene) in 60 to 70 per cent acid.[8] Reaction between the olefin and acid, especially with gaseous olefins, is increased and facilitated by use of increased pressures and by agitation in the presence of a liquid (for example, a high-boiling petroleum fraction) which is a solvent for the olefin but which is immiscible with the acid. Many different types of catalysts have been proposed which not only aid absorption of the olefin by the acid but also reduce losses due to polymerization.

Alcohols which are produced on a commercial scale by the sulphuric acid process are ethyl, isopropyl, secondary and tertiary butyl, secondary amyl, and secondary hexyl.

The use of the two lower alcohols, ethyl and isopropyl alcohols, as solvents and in pharmaceutical preparations is too well known to

require further comment. Unique uses for higher secondary and tertiary alcohols are in the purification of slack wax,[9] in paint removing compositions,[10] and as fuels for internal combustion engines.[11] Alcohols also serve as the basic materials from which esters may be obtained, while ketones are prepared by the oxidation or dehydrogenation of secondary alcohols.

It looks highly promising to bring about reaction between, say, ethylene and water to combine them directly as alcohol. So far as I know, however, this work, which has been carried on intensively in England particularly and largely by Imperial Chemical Industries, further by the Shell Company, has not indicated a promising yield of alcohol. The success of the operation, if it has any future, is now held to reside in the finding of a suitable catalyst.

In direct hydration of this nature a mixture of the olefin and steam is led over a catalyst at temperatures varying from 100° to 600° C., generally about 100° to 350° C. In most instances the ratio of hydrocarbons to steam is high, usually 8:1 or more. This ratio also governs, at least to some extent, the type of product obtained, alcohols being formed primarily when the ratio is high and ethers when the proportions of olefins and steam approach one another. Pressures from one to about 350 atmospheres have been advocated. The catalysts employed include metals and their alloys, metallic oxides and phosphates, non-volatile acids (e.g., sulphuric or phosphoric acid), and volatile organic acids (such as acetic acid).[12]

Esters

The combination of alcohols with acids, acid anhydrides, or acid chlorides are familiar methods for preparing esters. Of more interest is the reaction between olefins and acids to give esters.

Direct esterification of ethylene or propylene by organic acids is apparently difficult to effect. Esterification can be accomplished, however, by first absorbing the olefin in sulphuric acid and then treating the solution with either the organic acid or a salt of the acid.[13] The higher olefins are much more amenable to esterification. For example, butyl acetate is obtained on passing butylene, at temperatures of 50° C. or higher and under pressures of 100 to 180 pounds per square inch, countercurrent to a stream of glacial acetic acid containing some sulphuric acid.[14] Amylene may be esterified in a similar manner.[15]

Esters so obtained may serve as solvents for various gums and resins and in the preparation of lacquers.[16]

Ketones

As previously mentioned, dehydrogenation or oxidation of secondary alcohols leads to the formation of ketones. The general reaction may be written:

$$\begin{matrix} R' \\ R \end{matrix}\!\!>\!CHOH \rightarrow \begin{matrix} R' \\ R \end{matrix}\!\!>\!CO + H_2$$

Of the ketones, acetone is probably the most important industrially. It is a well-known solvent for cellulose esters, for many gums and resins, some waxes and fats. It is employed in the manufacture of smokeless powder, celluloid, and certain kinds of artificial silks, as well as in the scouring of wool. Mixed with toluene or benzene it yields a solvent which has been employed as a dewaxing medium for lubricating oils. As a solvent for acetylene, acetone has been employed on a large scale for the prevention of explosions during the storing of that gas.

Although acetone (and other ketones) has been produced largely by fermentation processes, isopropyl alcohol offers a convenient source for this ketone. Acetone is obtained by the dehydrogenation of this alcohol at temperatures of 250° to 430° C. in the presence of catalysts such as copper,[17] metallic sulphides,[18] or various salts of zinc, nickel, cobalt, iron, aluminum, calcium or magnesium.[19] Catalysts for the vapor-phase oxidation of isopropyl alcohol to acetone include copper,[20] brass,[21] silver,[22] and zinc oxide.[23] Many metallic oxides, such as manganese dioxide and barium peroxide, have been suggested also.[24]

Another ketone, which can be made from petroleum hydrocarbons and which now finds application as a solvent in the cellulose lacquer industry, is methyl ethyl ketone. The oxidation of secondary butyl alcohol, derived from butylene, offers a convenient method for preparing this ketone. It possesses a boiling point somewhat higher than that of acetone and due to its lower vapor pressure is less liable than

acetone to cause "blushing" in lacquers. Provided it could be made in quantity and sufficiently cheaply it would replace acetone as a solvent for many purposes.

From the foregoing discussion it will be seen that olefins in cracking gas can be made to unite (directly or indirectly) with water to yield alcohols, from which two main classes of derivatives are obtained, esters and ketones. Reverting again to cracking gas, it is found that the olefins present can be made to react with chlorine to give olefin dichlorides, or with hypochlorous acid to give chlorohydrins. From these latter compounds two other classes of derivatives are obtained, glycols and olefin oxides.

Chlorohydrins

Although ethylene chlorohydrin has been known since about 1859, it did not assume a position of importance until the World War when it was used in the manufacture of Mustard Gas.

One method of preparing ethylene chlorohydrin consists in passing ethylene into an aqueous solution of a hypochlorite from which hypochlorous acid is set free by the addition of a weak acid[25] (e.g., sodium hypochlorite and sodium bicarbonate or carbon dioxide). Passage of ethylene and chlorine concurrently into either water or an aqueous solution of a base, for example, sodium carbonate, either in the absence or presence of an immiscible liquid which serves as a solvent for the chlorohydrin, is another method.[26] In such operations the temperature is kept low, about 10° to 12° C., and the chlorohydrin concentration is maintained at about 6 to 10 per cent. Reaction in the vapor phase between chlorine, ethylene, and steam, employing catalysts such as manganese dioxide, chromates or ferric oxide, has been proposed.[27]

The chlorohydrins of propylene and butylene have been prepared similarly. With the higher olefins, particularly butylene and higher, a considerable proportion of dichlorides is formed which materially reduces the yields.

Chlorohydrins have been suggested as solvents for the extraction of aromatics, phenols, and sulphur and nitrogen compounds from brown-coal tar distillates,[28] for the preparation of wetting agents[29] (by condensation with amines), in the making of synthetic resins by esterifying with rosin[30] or by interaction with phenol alcohols,[31] and in the manufacture of lacquers and plastics.[32]

Ethylene Dichloride

Ethylene dichloride is made by the direct addition of chlorine to ethylene or to the ethylene fraction of cracking gas. With dry gases and at ordinary temperatures reaction is rather slow. It is much faster when carried out in the liquid phase, in the presence of catalysts or of solvents, or at high temperatures. Under the last named conditions it is difficult to limit the reaction as substitution products are also formed. Ethylene dichloride has been suggested as a solvent for this reaction.[33] Another method is to mix liquid chlorine with ethylene at 0° C.[34] The dihalide is also prepared by allowing a mixture of chlorine and ethylene to flow through a reaction tower countercurrent to a stream of water.

Ethylene dichloride is a heavy colorless liquid boiling at 83.5° C., melting at — 36° C., and having d^{20}_{4} 1.2569. It is only very slightly soluble in water, more so in alcohol and ether, and miscible with oils and fats. It burns with difficulty and its flames are readily extinguished. It is resistant to hydrolysis and oxidation, and may be used in metal containers at its boiling point with little danger of corrosion. Slow hydrolysis on exposure to light is prevented by addition of a small proportion of alcohol.[35]

This dihalide is employed as a fumigant, as a solvent and in the manufacture of ethylene glycol. As solvent it can be used in the extraction of oils, fats and resins, and mixed with methyl or ethyl alcohol will dissolve cellulose nitrate or acetate. It is also a good medium to be employed in the dewaxing of lubricating fractions,[36] as paraffin wax is only very slightly soluble in it at temperatures below 25° C. Either alone or mixed with carbon tetrachloride it is a cleaning agent.[37] On a volumetric basis it is a cheaper solvent than carbon tetrachloride and superior in its stability towards water and steam.

An interesting type of product derived from ethylene chloride is that designated by the term "Thiokol." [38] The latter is made by the interaction of the dihalide with the polysulphides of alkali or alkaline earth metals. Thiokol resembles soft rubber in properties, but is characterized by a high sulphur content and insolubility in practically all organic liquids. It can be incorporated with unvulcanized rubber and the mixture vulcanized. Vulcanized products are also insoluble in organic liquids, particularly petroleum distillates, and are used, for example, in the form of a hose, for handling such solvents.

Glycols

Hydrolysis of ethylene dichloride by dilute solutions of alkalies leads to the formation of ethylene glycol.[39] Another method for making this compound is by hydrolysis of ethylene chlorohydrin.[40] Direct oxidation of ethylene to glycol in the presence of water has also been employed. For example, ethylene and oxygen are introduced into water containing iodine (or compounds which readily liberate iodine, such as potassium triiodide or ferric iodide) and a manganese or iron oxidation catalyst.[41] Or, ethylene is treated with air and water at 150° to 300° C., under pressure, in the presence of metallic catalysts.[42]

Ethylene glycol is a colorless, odorless liquid and possesses a sweet taste. It boils at 197.5° C. and has a density of 1.115 at 20° C. It is miscible in all proportions with water, alcohol and many other solvents.

Possibly the most common uses of glycol are as a solvent and an anti-freeze for automobile radiators. In addition it is employed in the manufacture of cosmetics, in the preservation of anatomical and biological specimens, in the treatment of skins and furs, and as an aid in the finishing and dyeing of fabrics. Its many derivatives, however, have found industrial applications in diverse directions.[43] Thus, the monoethers (e.g., the monoethyl ether or "Cellosolve") are widely used in lacquers.[44] The nitrates form the basis for low-freezing dynamites.[45] Esters of glycols and polybasic acids (e.g., phthalic) are of resinous nature and are useful in lacquers.[46]

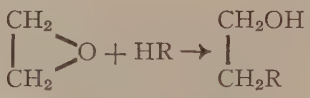
Higher-boiling materials, the so-called polyglycols, are formed as by-products during the making of glycols. These substances can also be made by dehydration of ethylene glycol or by the action of water on ethylene oxide. The lowest member, diethylene glycol, has proved to be an almost ideal lubricant for wool spinning.[47] Various derivatives of polyglycols such as the monoethyl ether of diethylene glycol or "Carbitol" have found varied applications.[48]

Olefin Oxides

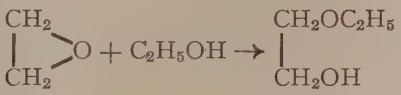
Olefin oxides, although classified as neutral substances, are capable of taking part in an astonishing number of reactions, and interest is centered chiefly in their derivatives rather than in the oxides themselves. Thus far only ethylene oxide appears to be utilized commer-

cially, although higher olefin oxides are known. These oxides are made by heating chlorohydrins with solid or anhydrous alkalies. They are also obtained on heating concentrated solutions of chlorohydrins with alkalies.[49] Ethylene oxide is said to be obtained on conducting ethylene, steam, air, and hydrogen over metallic catalysts at temperatures of 150° to 400° C.[50]

Ethylene oxide, and alkaline oxides generally, react with organic substances containing an easily replaceable hydrogen atom, e.g., alcohols, acids, phenols and amines, and also with water. These reactions may be represented by:



Glycol monoethers are made by the reaction of ethylene oxide, or other aliphatic oxide, with an alcohol.[51]



Catalysts for this reaction include sulphuric acid,[52] the sulphates of nickel, zinc or chromium,[53] hydrosilicates of aluminum,[54] and dialkyl sulphates.[55] When an excess of the olefin oxide is employed it is possible to make polyolefin glycol ethers. For example, the introduction of ethylene oxide into anhydrous ethyl alcohol containing a small amount of sodium (as a catalyst) leads to the formation of the ethyl ether of tetraethylene glycol and higher polyglycols.[56] The monoalkyl ethers are solvents for cellulose nitrate, resins, gums and oils. They are miscible with organic solvents, and the lower ethers are soluble in water. The methyl ether is a solvent for cellulose acetate, and is especially adapted to the preparation of lacquers.[57]

Ethanolamines

Ethylene oxide reacts with aqueous ammonia to yield a mixture of three basic substances, mono-, di-, and tri-ethanolamines, which

can be separated by distillation.[58] The proportions of the three products depend largely on the relative proportions of the reactants, an excess of ethylene oxide favoring the formation of triethanolamine. The boiling points of the ethanolamines are as follows:

Monoethanolamine, $NH_2CH_2CH_2OH$, 171° C. at 757 mm.
Diethanolamine, $NH(CH_2CH_2OH)_2$, 217° C. at 150 mm.
Triethanolamine, $N(CH_2CH_2OH)_3$, 277° C. at 150 mm.

The ethanolamines are miscible in all proportions with water, alcohol, acetone, glycerol, and ethylene chlorohydrin, but not with ether and some aldehydes.

Monoethanolamine is a colorless, slightly viscous, hygroscopic liquid, with a faint ammoniacal odor. Diethanolamine is a colorless, odorless liquid, with a viscosity similar to that of glycerol. The dinitrate of monoethanolamine[59] and the trinitrate of diethanolamine[60] have been proposed as explosives. Pure triethanolamine is a white crystalline solid at room temperature. The commercial product is a clear, viscous, hygroscopic liquid, of d_4^{20} 1.124, soluble in most organic liquids containing oxygen, but only very slightly soluble in hydrocarbons.

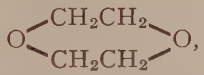
In the Girbotol process, aqueous solutions of a mixture of the ethanolamines, particularly the di- and tri-ethanolamines, are employed for the removal of carbon dioxide and hydrogen sulphide from gases.[61] The carbonates and acid sulphides readily decompose at temperatures above 50° C. with regeneration of the solvent. The ethanolamines form stable salts with sulphur dioxide and therefore are unsuitable for the removal of that gas.

Many other uses have been suggested for these amines, as for example, extraction agents for the refining of mineral oils,[62] plasticizers for cellulose esters,[63] catalysts in the formation of phenol-aldehyde condensation products,[64] preservative agents in rubber compositions,[65] and stabilizers for lead tetra-alkyls.[66]

Ethanolamines combine readily with fatty acids to yield soaps[67] whose consistency depends primarily upon the acid employed. The oleates have the consistency of petroleum jelly, while the stearate is a hard wax-like solid. These soaps are soluble in water, benzene, toluene, turpentine, but only slightly so in lubricating and petroleum

oils. The oleate possesses emulsify properties and may be used for promoting oil-in-water emulsions.

Dioxan

Diethylene dioxide, or dioxan,  , although structurally related to ethylene oxide, should more properly be considered as a derivative of ethylene glycol. It is made industrially by heating ethylene glycol with dehydrating agents, such as sulphuric acid,[68] or anhydrous ferric sulphate.[69] Similarly, dimethyldioxan is obtained from 1,2-propylene glycol and diethyldioxan from 1,2-butylene glycol.

Dioxan is a liquid boiling at 102°C. and melting at 11°C. It is soluble in water and in many of the usual organic solvents. It is a solvent for resins and fats and also for cellulose esters.

Production of Unsaturated Hydrocarbons

The action of heat on saturated hydrocarbons results in the formation of unsaturated compounds, and also in many instances leads to a rearrangement within the molecule. Perhaps the largest source of unsaturated hydrocarbons is cracking gas, the composition of which has already been discussed. Butadiene is a component of vapor-phase cracking gas. Acetylene is formed from hydrocarbons at temperatures considerably above those employed in cracking. These two unsaturated compounds are of particular interest.

Acetylene

Acetylene is one of the thermal decomposition products of hydrocarbons at high temperatures, 800°C. or above. Below this temperature it is not formed, or only in very small proportions (methane, for example, requiring temperatures of 1000°-1200°C.). It is made by the thermal decomposition of practically all hydrocarbons in the electric arc. Generally better yields are obtained from low-boiling or gaseous petroleum hydrocarbons than from the higher-boiling distillates. Short periods of heating, reduced pressure and the addition of hydrogen or steam to the gaseous hydrocarbons minimizes their decomposition to carbon and hydrogen.

An important reaction of acetylene is its hydration to acetaldehyde

which can be subsequently converted to acetic acid. Hydration can be conducted in either the liquid or gaseous phase. In liquid-phase operations, a stream of acetylene is passed through dilute sulphuric acid (about 6 per cent) to which has been added mercuric oxide, the mercury salt thus formed serving as a catalyst. Reaction proceeds with the evolution of heat, and vaporized acetaldehyde is carried along in the gas stream from which it can be recovered by cooling. Oxidation of the aldehyde readily yields acetic acid. A large number of by-products [70] are formed in minute amount in the hydration of acetylene. One of these, diacetyl, is used for flavoring butter substitutes.

A difficulty encountered in vapor-phase operations is the ease with which acetaldehyde is converted to other substances, e.g., crotonaldehyde or esters. This is overcome by the addition of a gaseous oxidizing agent, for example, by conducting acetylene, steam and oxygen, at 100° to 200°C., over a catalyst consisting of a mercuric salt.[71]

Acetylene is being produced at a refinery in this country by arcing hydrocarbon gases and is used for making acetic acid. Thus petroleum has definitely become a source of another hydrocarbon, acetylene.

Other important derivatives of acetylene are vinyl esters and acetylene polymers.

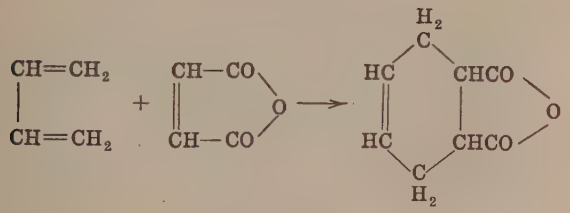
Vinyl esters are obtained from acetylene and acids, the reaction occurring by direct addition in the presence of a mercury catalyst. Vinyl esters can be transformed by various methods into very light-colored resins ("Vinylite") which at present are finding rather wide utilization in coatings and plastics, particularly in phonograph records.

Of the various polymers of acetylene, one type is formed by the action of heat on the hydrocarbon in contact with certain metals. This is known as cuprene and is an insoluble, brown, amorphous solid.[72] Another type includes liquids obtained by absorption of acetylene in solutions of cuprous salts. Mono- and divinylacetylene are thus formed. Divinylacetylene slowly thickens to a viscous liquid which, after application as a film, hardens further to an insoluble coating.[73] Monovinylacetylene, when combined with hydrochloric acid, forms the liquid called chloroprene.[74] This liquid can be transformed very readily into an elastic solid which resembles natural rubber more closely than does any other synthetic material. Acetylene rubber of this type is known as DuPrene.

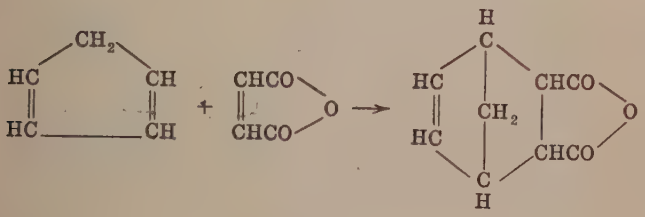
Butadiene

Butadiene is a gaseous product of the pyrolysis of hydrocarbons at temperatures just below those at which transformation of straight-chain hydrocarbons to aromatics takes place. To illustrate, the maximum yield of butadiene from ethylene is obtained at 750°C.,[75] from propane, propylene and butane [76] at about 727°-728°C., and at 654°C. a large yield is secured from cyclohexane.

An interesting reaction of butadiene, and other conjugated diolefins, is that with maleic anhydride to yield cyclic acid anhydrides.[77] This reaction may be represented by:



Such products are often readily formed by allowing the diolefin and maleic anhydride to react in the presence of benzene. Not only aliphatic but also cyclic diolefins, e.g., cyclopentadiene, exhibit this reaction.



By this reaction it has been shown that butadiene, piperylene, isoprene, and cyclopentadiene were present in the low-boiling fractions of a high-temperature cracked gasoline.[78]

Butadiene and similar diolefins have been considered for some time as a source of artificial rubber.[79] When heated with various substances which act as catalysts, butadiene polymerizes and forms

a solid mass possessing some of the properties of rubber. Considerable work has been done recently on this reaction but the development is hampered by economic considerations. However, a resin suitable for varnishes has been produced from the diolefins of vapor-phase cracked distillates by the polymerizing action of aluminum chloride.[80] This petroleum resin produces varnishes which dry very rapidly. Another related material is a dark-colored liquid product consisting of a mixture of polymerized olefins and diolefins and known as "Puresinol."[81] This is made as a by-product in the refining of highly cracked gasoline distillates and is proposed as a substitute for linseed and other drying oils. Its specific gravity is 0.956, its viscosity (Saybolt universal at 100°F.) is 200 seconds, and its iodine number is 175. Brittleness of the dried film would appear to limit its uses.

Aromatics

Certain crudes, particularly Borneo petroleum, contain aromatic hydrocarbons to some extent. Aromatics are also formed in cracking processes. However, in the manufacture of "Hydrosolvents" by hydrogenation it has been found that aromatic compounds are produced in large proportions.

If an overhead cut is made of such Hydrosolvent, the following results roughly express the proportion of aromatic hydrocarbons:

200-275°F.	10%
275-365°F.	35%
365-419°F.	38%
419-460°F.	8-10%

Distillate under 200°F. end point is added to gasoline.

The increase in aromatic content with the boiling point is of significance in the coating industry, since a coating in which such solvent is present as the thinning agent becomes richer in more powerful solvents as evaporation increases. This tends to permit the binder in the composition to satisfactorily orient giving an unusually hard and glossy surface.

In the crude Hydrosolvent cut there is probably about 1% benzene, 4% toluene, 18% xylenes and 25% of the trimethylbenzene type of hydrocarbons, including mesitylene and isomers, such as methylethylbenzene, propylbenzene, etc. There are also indications of the

presence of hydrogenated naphthalenes, tetralin and decalin particularly. There may be also some octalin. While a small proportion of actual naphthalene is present, it is likely to be negligible in amount.

The hydrocarbons from coal tar are characterized particularly by the insignificant proportions of trimethylbenzene hydrocarbons and the high yield of these through hydrogenation of petroleum appears to fill a gap not supplied by coal tar. In other words, coal tar yields benzene, toluene and xylene and then rather suddenly there is a jump to naphthalene, anthracene, and other polycyclic hydrocarbons. Hydrogenation, therefore, should serve as a means to place the petroleum industry in the coal-tar field in those places where coal tar is lacking.

Oxidation Products

The oxidation of high molecular weight petroleum hydrocarbons, particularly paraffin wax, is a method for the preparation of high molecular weight acids. Air, oxygen, ozone, the oxides of nitrogen and nitric acid can be used as the oxidizing agents, though air is most generally employed. Oxidation is carried out at temperatures above the melting point of the wax, usually about 160° to 180° C. Catalysts for oxidation include metallic oxides,[82] inorganic salts of organic acids, e.g., barium stearate or calcium cinnamate,[83] manganese acetylacetonate[84] and naphthenate.[85]

Separation of the acids from the reaction product is accomplished by extraction with alcohols [86] or with alkalies,[87] by sweating,[88] i.e., partial liquefaction of the product by heat followed by pressing to separate the liquid and solid portions, and by distillation under reduced pressure.[89]

These acids are designated "wax acids," as this term indicates wax as their source rather than fats, and also some investigations have intimated that these acids contain a large proportion of substances having an uneven number of carbon atoms per molecule as contrasted with fatty acids which contain an even number of carbon atoms. Wax acids can be employed in the manufacture of synthetic fats by esterification with glycol or glycerol,[90] and of soaps. The latter is the most important use. Instead of wax acids, higher alcohols can also be obtained by use of the proper catalyst. Sulphation of these wax alcohols forms soaps of the hard-water type, a procedure which appears cheaper than making detergents from the alcohols of vegetable oil hydrogenation.

In addition to high-molecular weight acids, low-molecular weight or water-soluble acids are also obtained by oxidation as well as intermediate oxidation products such as aldehydes, ketones, esters, acid anhydrides, and hydroxy acids. In preparing alcohols the wax is oxidized for a shorter time than that employed making acids. The catalysts which are particularly useful in this reaction are acetic acid or weak inorganic acids such as boric acid.[91] The alcohols are separated from the reaction products by distillation under reduced pressure with steam.

Chlorination Products

Although a vast amount of work has been reported on the chlorination of saturated hydrocarbons, only brief mention can be made of some of the products obtained.

Chlorination of methane, for example, yields methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). Methyl chloride, because of its low boiling point has been suggested as a refrigerant. The remaining three substances can be used as solvents, chloroform to a limited extent as an anesthetic, and carbon tetrachloride as a fire-extinguisher. Carbon tetrachloride and antimony trifluoride react to give dichlorodifluoromethane, a substance particularly applicable as a refrigerant because of its low toxicity.

Chlorination of natural-gas gasoline gives a mixture of amyl chlorides, which can be hydrolyzed to a mixture of amyl alcohols,[92] the latter being marketed under the name of Pentasol, or esterified with acetic acid (Pentacetate).

The production of Paraflow is an outstanding development in the utilization of chlorinated petroleum hydrocarbons. Paraffin wax is chlorinated until its chlorine content is about 10 to 12 per cent. The chlorinated wax is then reacted with benzene, naphthalene or anthracene in an inert solvent (e.g., kerosene) at 140° to 160°F., using aluminum chloride as a catalyst. After reaction is completed, the aluminum chloride sludge is withdrawn, and the solvent and excess wax removed by distillation, the latter under reduced pressure. The product is a *chlorine-free,* synthetic hydrocarbon oil possessing the unusual property of lowering the pour point of wax-bearing lubricating oils. For example, the addition of 1 per cent of this synthetic oil to a crude Pennsylvania lubricating oil lowered its pour point from

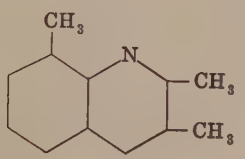
+30°F. to below —5°F. The utilization of Paraflow, therefore, eliminates the severe dewaxing operations required in the refining of many lubricating oils.[93]

Nitrogen Compounds from Petroleum

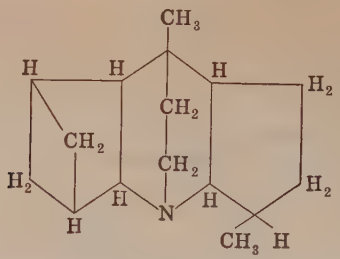
In coal oil and shale oil there are present aromatic compounds of nitrogen whose identification has been accomplished with comparative ease. The reverse is true with respect to petroleum, for here is presented an astonishing variety of nitrogen compounds of unknown structures. Some of them, according to our present knowledge, fall into the class of hydroaromatics. Hydroaromatics are closely related to alkaloids and to change hydroaromatic bases to alkaloids it is only necessary that the proper placement of oxygen be made. A brief mention is therefore made of these nitrogen compounds as opening up a new field of scientific interest and possible practical value.

The nitrogen content of crude petroleum oils is rather low, about 0.1 per cent or less, though some California oils have shown as high as 0.82 per cent.[94] Apparently the nitrogen compounds in crude oils are non-basic, and are not extractable with acids. The distillates from such crudes, however, contain nitrogen bases, together with inert nitrogen compounds, thus indicating a decomposition of rather complex nitrogenous substances during the distillation operation.[95]

To illustrate the type of compounds which have been isolated only two need be mentioned. Both of these were isolated from a sulphur-dioxide extract obtained in the refining of kerosene. From the fraction boiling at 276-277°C., 2, 3, 8-trimethylquinoline was obtained.



A hydroaromatic base, $C_{16}H_{25}N$, from the same fraction, is of interest in that it represents a compound of the cyclopentane type. The structure assigned to this substance is:



This has been named decahydro-3, 8-dimethyl-5, 7-methano-4, 8-ethanopyrindacine.

So far there is no explanation why hydroaromatics should be in petroleum and absent from coal, shale and bone distillates. Furthermore, none of the bases isolated from petroleum has been obtained from other natural sources.

Sulphur Compounds from Petroleum

The sulphur content of crude oils from different localities varies widely, ranging from less than 0.2 per cent to as high as 4 to 5 per cent.[96] Practically all of the simpler types of sulphur compounds have been identified in such oils; these include mercaptans, thioethers, thiophenes, thiophanes, organic sulphides and disulphides, compounds containing both sulphur and oxygen, as well as hydrogen sulphide, elemental sulphur, and carbon disulphide.[97] From the refiner's view these sulphur-containing substances are impurities which, because of their corrosive properties or their odors, must be removed particularly from the gasoline and kerosene fractions. To the chemist, however, the isolation and utilization of these substances opens a field of wide possibilities.

Hydrogen Sulphide

Hydrogen sulphide may be extracted from petroleum or its distillates, or from the gases from the distillation or cracking of high sulphur crudes or distillates, by solutions of alkalies, for example, sodium hydroxide, sodium carbonate and bicarbonate, or ethanolamines. Aqueous suspensions of brucite [98] have been suggested for the same purpose. Hydrogen sulphide may be liberated, except in the case of sodium hydroxide, by heating the solutions or suspensions.

The uses of gaseous hydrogen sulphide, other than in the laboratory, appear to be rather limited. It does react, at high temperatures, with olefins or acetylene in the presence of catalysts to yield mercaptans, thioethers, thiophene and its derivatives, and carbon disulphide.[99] When hydrogen sulphide is mixed with methane, ethane, or propane and the mixture heated to 1200°C., both benzene and carbon disulphide are obtained.[100] The salts of hydrogen sulphide, particularly the sodium salt, have been used as aids in dyeing, as reducing agents, depilatories, and denitrating agents, and in the manufacture of sulphur dyes and lithopone.

The preferential oxidation of hydrogen sulphide to sulphur, either by metallic oxides or by sulphur dioxide, are well-known processes and suggest the possibility of hydrogen sulphide as a potential source of sulphur.

Mercaptans

Aqueous solutions of sodium hydroxide and alcoholic solutions of sodium plumbite [101] or of sodium or potassium hydroxide [102] have been suggested for the extraction of mercaptans from petroleum distillates. As an industrial method the use of aqueous sodium hydroxide is probably to be preferred, and mercaptans may be liberated from such by steam distillation.[103]

Because of secondary reactions occurring during distillation, some disulphides may be obtained at the same time. These can be readily reduced to mercaptans, or separation of mercaptans and disulphides effected by the use of alkalies.

Mercaptans have been suggested as pickling inhibitors [104] and as intermediates in the preparation of dyes. Heated with phosphorus tri- or pentasulphide mercaptans yield liquids which may be employed in ore-flotation processes.[105] The well-known soporific sulphonal is the sulphone of the mercaptole obtained from acetone and ethyl mercaptan. Because of their penetrating odor, volatility, and insolubility in water, the lower-boiling mercaptans, especially ethyl mercaptan, have been used for detecting leaks in gas mains.[106] A product designated Cal-Odorant, apparently a mixture of hydrocarbons and sulphur compounds, is marketed for odorizing natural gas.[107] Butyl mercaptan is said to be a stabilizer for chlorinated hydrocarbons, e.g., carbon tetrachloride or tetrachloroethylene.[108]

Thioethers

Apparently little work has been reported on the isolation of thioethers from petroleum. Possible methods for the recovery of this class of sulphur compounds include the formation of addition compounds with salts, e.g., mercuric iodide or chloride, titanium tetrachloride, or platinic chloride, and their extraction from acid sludge. Passage of mercaptans over metallic catalysts (sulphides of cadmium or zinc, and aluminum chloride) at temperatures of 320°-350°C. results in the formation of thioethers.[109]

Thioethers are solvents for rubber, and for resins such as abietic acid, paracumarone, petroleum resin, and m- and p-cresol-sulphur chloride resins. Ethyl alcohol and ethyl sulphide or methyl alcohol and propyl sulphide form solvents for cellulose nitrate. Ethyl sulphoxide, an oxidation product of ethyl sulphide, has been suggested as a plasticizer for pyroxylin.

Sulphonates

In the refining of mineral oils, particularly in the production of white pharmaceutical petrolatum (vaseline oils), with sulphuric acid, a certain amount of sulphonation occurs.[110] Most lubricating oils contain reactive hydrocarbons which are partly removed from the oil by agitation with sulphuric acid. Such refining operations produce sludges which usually contain free acids, polymerized bodies, asphaltic materials, and oxidized substances together with various sulphonated products. The disposal of this acid sludge has long been a problem to the refiner. The acid is usually separated by the addition of water and reconcentrated for further treatment of distillates. The residual material is largely used as a fuel.[111]

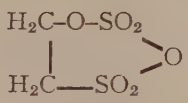
Numerous methods have been devised for the removal of the sulphonic acids from sludges. In general, separation is effected by some selective action such as that of solvents or adsorbents or by salting-out of the acids in the form of their alkali or alkaline earth salts. As is quite evident, the sulphonic acids vary with the character of the sludge, the type of the original oil and the refining treatment, hence the methods used for their recovery are generally adapted to a particular material.

Mineral oil sulphonic acids, varieties of which are known as Kontakt, mahogany acids, and green acids have found commercial interest. They have been proposed as detergents, reagents for hydro-

lyzing fats to glycerol and acids, and textile reagents, i.e., wetting, penetrating, cleansing or lubricating agents in textile treatment. On some types of dispersions mineral oil sulphonic acids act as stabilizers but on others they exert a coagulating effect. In the petroleum industry the acids recovered from sludges have been used to prevent emulsification in subsequent refining operations. Various sulphonated mineral oil fractions have been employed also in insecticide compositions. These applications have been so extensively investigated that to single out one as an illustration would be injudicious to several hundred others.

The sulphonated mineral oils can be considered to consist largely of sulphonated paraffin and cycloparaffin (naphthene) hydrocarbons and to be derived from petroleum distillates. Aromatic sulphonic acids, though they may be formed also in small quantities in petroleum refining, are largely derived from coal tar. The petroleum sulphonic acids can thus be looked upon as by-products, whereas another series of materials derived from olefins resulting from pyrolysis of petroleum distillates, for example, can be considered to be principal products.

When ethylene reacts with anhydrous sulphur trioxide, a crystalline compound, which melts at 80°C., is formed. This substance is carbyl sulphate,



It dissolves in water with the liberation of heat and the formation of ethionic acid, $HO_3S{\cdot}C_2H_4{\cdot}OSO_3H$, and isethionic acid, $HO_3S{\cdot}C_2H_4{\cdot}OH$. Salts of ester-like condensation products of fatty acids, for example oleic acid,[112] have appeared as Igepons,[113] and have received much attention as wetting and cleansing agents, especially in textile treatment. Olefins resulting from the destructive oxidation of paraffin wax and naphthenic acids have also been sulphonated to give similar products.[114]

Though petroleum sulphonic acids have been known and investigated for a long period, great technical interest was not manifested until recently with the development of products of superior detergent quality. The sulphation of olefins, resulting from the cracking of

petroleum, has opened a wide field for the petroleum industry and further developments quite as remarkable are already foreshadowed.

Naphthenic Acids

Other by-products from the refining of petroleum distillates are naphthenic acids. These acids are extracted from the distillates by the alkali wash which may be the only treatment required in refining or which may follow a preliminary acid treat. The acids are obtained in the free state by acidifying the alkali with sulphuric acid or with sulphur dioxide. Their name is indicative of the fact that they were first derived from naphthene- (or cycloparaffin-) containing crude oils. Later investigations of the structures and properties of these acids have shown also that they bear a chemical relation to the naphthene hydrocarbons, particularly to cyclopentane.

An interesting application of the heavy metal salts of these acids, the cobalt, lead, and manganese salts especially, is as paint and varnish driers.[115] Solutions of such salts in hydrocarbons are known as "Soligen" driers. Linseed oil varnishes, containing 0.14 to 0.29 per cent cobalt naphthenate dry in 1 to 10 per cent less time than those containing a resinate drier.

The sodium salts of these acids have been suggested as soaps. Their detergent action and lathering power are inferior to those of sodium palmitate or toilet soaps of mixed fatty acids. A 40 per cent solution of such soaps can be cooled to 0° C. for thirty minutes without effecting complete solidification, thus indicating their possible use in the preparation of neutral soft and liquid soaps. Much larger quantities of sodium chloride are required to salt out sodium naphthenates from aqueous solution than is required with coconut oil soap.[116]

Hydrogen

According to well-known processes, hydrocarbons and steam react at high temperatures in the presence of catalysts to give hydrogen and the oxides of carbon. With methane the reactions may be represented by

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

and for higher hydrocarbons by the general reaction

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$$

These reactions are reversible, the equilibrium depending upon the temperatures and pressures employed. From an industrial point of view the chief interest in them lies in the cheap production of hydrogen from gaseous hydrocarbons, as more hydrogen can be obtained from a given quantity of methane, or other hydrocarbons, by these reactions than by purely thermal decomposition. For example, the thermal decomposition of one volume of methane yields two volumes of hydrogen

$$CH_4 \rightarrow C + 2H_2$$

while according to the above reactions it is possible to obtain as high as four volumes of hydrogen from one volume of methane.

Application of the above reactions is illustrated in the preparation of hydrogen from cracking gas and steam by a two-stage process.[117] In the first stage, reaction between the gases takes place at about 870°C. (1600°F.). The resulting mixture of hydrogen and carbon monoxide is further mixed with steam and conducted over a catalyst at a temperature of about 455°C. (850°F.). By this second step an additional supply of hydrogen is obtained by the conversion of carbon monoxide into carbon dioxide according to the well-known water-gas reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

At the end of these two stages the gaseous mixture contains about 79 per cent hydrogen, 20 per cent carbon dioxide, and 1 per cent of other gases. Carbon dioxide is removed by compressing the gases to a pressure of 240 pounds per square inch followed by washing with water and finally with aqueous triethanolamine. The product then contains more than 97 per cent hydrogen and can be used in the hydrogenation of oils.

The hydrocarbon gases should be free of hydrogen sulphide, or other sulphur compounds, which are poisons for the catalysts. The latter often consist of the oxides of nickel, cobalt, iron or aluminum to which may be added activators, such as the oxides of chromium, vanadium, or magnesium.[118]

Natural Gas

Natural gas, which may be regarded as gaseous petroleum, consists primarily of methane, together with ethane, and propane, small quantities of butane, pentane and other paraffins up to octane, and smaller proportions of carbon dioxide, hydrogen sulphide, and (in some instances) helium. Natural gas is roughly divided into two classes, "wet" and "dry" gases, the former containing a large proportion of easily liquefiable hydrocarbons. Removal of these higher paraffins from natural gas by (1) compression, (2) absorption in oil, (3) or by adsorption, for example with charcoal, yields natural-gas gasoline. Before blending this product with other motor fuels it is subjected to stabilization, or distillation under pressure, by which propane and some butanes are obtained. This propane-butane fraction is utilized as a fuel for domestic purposes, in the enrichment of manufactured gas, as a substitute for acetylene in welding. Natural gas is utilized primarily for the large-scale production of carbon black.

It is evident from the preceding discussion that a chemical industry dependent upon petroleum as a raw material is becoming well established. With the large number of possibilities offered by such a multitude of already available substances, future developments may be even more surprising. The chemistry of petroleum derivatives has indicated to us new sources of hitherto unavailable industrial chemicals and products.

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Discussion

Chairman Marshall: Discussion on the paper is now open.

H. K. Moore: This is hardly in connection with the paper, but Mr. Ellis showed some remarkable pictures of the absence of color, and I wish to know if they have ever tried the Cottrell Process to remove the carbon from the gases, which seems to me might be used to good advantage.

CARLETON ELLIS: You mean such as the Cottrell separator?

H. K. MOORE: Yes.

CARLETON ELLIS: I believe that has been tried out, but I do not know just what the outcome was. It seems to me there was some short circuiting.

H. K. MOORE: At LaTuque we have quite an amount of his finely atomized carbon black. When you turn on the Cottrell the result is just the same as if you had cut it off with a knife. It is absolutely clear.

One other question I should like to ask although it is hardly germane to this paper is: what is the percentage of oil coke from say a barrel of crude?

CARLETON ELLIS: I do not know as it varies greatly in different processes.

P. H. GROGGINS: I should like to ask Mr. Ellis if he has formulated any opinion regarding the competitive position of the petroleum industry for the manufacture of acetic acid. He mentioned several processes in which the petroleum industry is interested and their possible competition with the ordinary acetylene and acid aldehydes process.

CARLETON ELLIS: I hesitate to say much about that. The principal point, as I see it, is this: When we think of acetylene, we think of calcium carbide, calcium carbide being lime. Now here no lime enters the picture. We have to use electrical power. The same is true in the case of carbide and I think it is a matter that has to be given further study before anyone can pass an opinion from an engineering standpoint.

CHAIRMAN MARSHALL: Is there any further discussion? If not, this is the end of the morning's technical session and the meeting will now adjourn.

INDUSTRIAL DEVELOPMENTS IN HEAT TRANSFER WITH ORGANIC COMPOUNDS

By R. LYMAN HEINDEL, Jr.*

Indirect heating has been accomplished by steam, hot gases, oils, a number of organic compounds and mercury. Each of the materials used in this manner has its own practical temperature range, above and below which it is unfitted for efficient, economical service.

In recent years the manufacture of many chemical compounds has been made possible through the proper application of high temperatures at low pressures with the assistance of one or more of the newer indirect heating media. We will review briefly the properties and limitations of some of these proposed heating fluids, and will then describe a number of installations which employ high-boiling-organic compounds as the source of heat.

Saturated steam has a practical and economical upper temperature limit in the neighborhood of 450°F., which corresponds to a pressure of approximately 400 pounds per sq. in. At temperatures in excess of 450° it is desirable to employ other heat transfer materials, whether they be liquid or vapor.

Where temperatures above 750° are to be encountered in the system, and it is desired to heat by means of a vapor, mercury is today the logical material to use. Although mercury costs in the neighborhood of $100 per gallon, it is an element, and in the absence of oxidizing conditions, is capable of operation at temperatures several hundred degrees higher than any known organic compound. There is a gap remaining between the uppermost practical temperature with high pressure steam and 674° F., the point of condensation of mercury vapor at atmospheric pressure.

Some of the organic heating materials which have been proposed during the last few years[4] are Anthracene, Phenanthrene, Naphthalene, Diphenyl, Diphenyloxide, certain specially selected oils and a series of mixtures under the name of Dowtherm. Each of these

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materials has certain advantages and certain disadvantages which we will briefly consider.

For a number of years, certain oils have been used as heat transfer fluids. These materials are limited in practical applications to temperatures below 600° F., and even in this range are quite viscous. They flow sluggishly, leaving a sludge or carbon-like deposit on heat exchange surfaces. The over-all efficiency of such a fluid is very low. Such oils may be purchased for approximately 80 cents a gallon.

Anthracene and phenanthrene have never been seriously considered because they are not commercially available in sufficient quantities. Published thermal data on phenanthrene were obtained from especially prepared laboratory samples.

Naphthalene is a definite compound, having the formula $C_{10}H_8$ and a melting point of 176° F. While it boils at 423° F., the most serious objection to its use is its tendency to sublime. Naphthalene is quite cheap, selling from 5 to 8 cents per pound, depending upon the quality and quantity.

Several years ago Dr. H. H. Dow[1,25] proposed the use of diphenyloxide in bi-fluid power plants. Other possible applications of diphenyloxide have been described by Roe[6] and Grebe.[9, 13] For other discussion see references 6, 8, 9, 10, 12, 15, 16, 17, 20, 23. This material is properly referred to as phenyl ether and has the formula $(C_6H_5)_2O$. It has a melting point of 80° F. and boils at 496° F. It is available at prices from 16 to 20 cents per pound, depending upon quantity.

Diphenyl, $C_{12}H_{10}$, was developed commercially even more recently than diphenyloxide. Diphenyl has a melting point of 154° F. and a boiling point of 491° F. (2, 3, 5, 11, 13, 15, 18, 20, 21).

It is quite obvious that with equivalent boiling points and with corresponding vapor temperature ranges, the most desirable materials for use as transfer agents are those which remain liquid at room temperature. It is our belief that at the present time there are only two practical heat transfer media for operation in the range 450 to 750° F. These fluids are the eutectic mixtures of diphenyloxide with diphenyl or with naphthalene, known as Dowtherms A and B respectively.

Mixtures of diphenyloxide and diphenyl composed of as much as 37% of the latter, are characterized by melting points lower in all cases than either diphenyloxide or diphenyl alone. The minimum freezing point mixture is obtained with 73½% of diphenyloxide and

26½% of diphenyl.[19, 22] This mixture has a freezing point of 53.6° and is designated as Dowtherm A. Dowtherm pipes do not have to be steam-jacketed, as it will not crystallize at room temperature, as will diphenyl and other compounds proposed for heating.

A similar eutectic mixture of diphenyloxide and naphthalene composed of approximately 85% of the former and 15% of the latter, and having a freezing point of 61° F., is designated as Dowtherm B. The boiling range of Dowtherm B is not quite as wide as that of Dowtherm A, and the freezing point, as will be observed, is somewhat higher.

Dowtherms A and B, in common with diphenyl and diphenyloxide, sell at a price between 16 and 20 cents per pound, depending upon the quantity. Their use, and exceptional properties which make them desirable for such use, will be described in the following portions of this paper.

If circulating liquids are desired which do not have the sludging characteristics found in oil, it is recommended that Dowtherm C, a very high boiling material capable of application up to 800° F., be employed. If a non-flammable agent for liquid-phase heat transfer is desired at temperatures not to exceed 650° F., it is recommended that Dowtherm D be used. For the purposes of this paper, however, we will restrict ourselves to the discussion of Dowtherm A.

Dowtherm is Non-Hazardous to Health

Economically, it is desirable that whatever heat transfer material is selected be retained within the system and that losses be eliminated. Every engineer is aware, however, of the difficulty of attaining a completely closed boiler system and of eliminating all losses. In view of this fact, we are frequently asked what the toxic effect of Dowtherm will be on workmen coming in contact with the escaping material. The constituents of Dowtherm A have both become well known to the chemical industry during the last few years. In all the time that diphenyloxide has been produced, there has been no evidence of any injurious effect from inhaling its vapors. As a matter of fact, diphenyloxide has been used for a number of years as a constituent in perfume. In liquid or crystalline form it is entirely without the irritant or corrosive action of phenol and has no injurious effect whatever on the skin. If it should accidentally get into the mouth or eye, Dowtherm produces a slight burning sensation for a short time,

somewhat similar to the effect of kerosene, but beyond that it shows no harmful results. In one instance in our plant a diphenyloxide release valve suddenly blew open, expelling vapors directly into a man's face. The only effect of this experience were those due to the temperature of the vapors. Although the vapors were hot, the burn was not serious, probably because no condensation could occur, the escaping vapor absorbing heat by expansion and no latent heat being

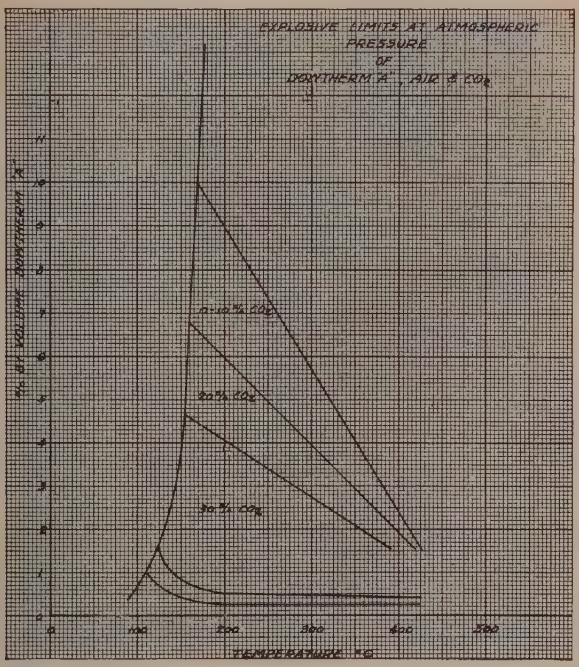

FIG. 1. Explosive limits at atmospheric pressure of Dowtherm A, air and CO_2.

liberated. The workman exposed to these fumes did not even experience a headache as a result of the exposure.

The possibility of combustion is another hazard which exists in the use of organic heat transfer materials. Dowtherm will burn, especially at elevated temperatures. Good engineering practice in the use of Dowtherm calls for equipment with all welded joints, or at least with sufficiently tight joints to eliminate losses. If losses occur through

small leaks in the system and if a source of ignition is present, the vapors will burn as though coming from a jet, and will not have any tendency to explode. In case of a leak in the furnace compartment, the high percentage of carbon dioxide would prevent the occurrence of an explosion. Fig. 1 defines the explosive limits of Dowtherm, carbon dioxide and air. It will be observed from this chart that the hazard is particularly small. In the boiler unit the gas temperature will usually be in excess of the upper explosive limit of Dowtherm, so that escaping vapors might ignite, but could not explode.

Stability

When the proposal was first made eight or nine years ago that diphenyloxide be used in generating steam at temperatures from 600 to 750° the objection was immediately raised that the material would be unstable at these temperatures. The late Dr. Dow in 1926 pointed out [1] reasons why this could not be a serious objection. Experiments have been conducted on both laboratory and plant scale to determine the life of Dowtherm under extreme conditions of temperature and pressure.

The most serious operating condition for Dowtherm is that in which there is an oxidizing agent or an excess of oxygen. It was under such a condition that the following tests were made. We have found that there is sufficient correspondence between the data obtained when testing diphenyl and those obtained for Dowtherm to assume that the following table applies to all products which have been classified roughly as diphenyl-type heat transfer materials. The Bremo Station has operated for three years with a Dowtherm temperature of 650° and with less than 2% breakdown of Dowtherm in the three years.

TABLE I. THERMAL DECOMPOSITION OF DOWTHERM IN THE PRESENCE OF AIR

Temperature	Decomposition per month, 20 working days 24 hours each
650° F.	.25— .35%
700	.4 — .6 %
725	1.1 — 1.6 %
750	approx. 3.3 — 5.0 %
775	approx. 7.0 —10.0 %

In the customary Dowtherm application where temperature is being carefully controlled through the regulation of pressure, the ac-

cumulation of decomposition products or of polymers having even lower vapor pressures than Dowtherm will materially affect the accuracy of such pressure temperature regulations. Laboratory tests, confirmed by actual plant experience, point to the fact that when the accumulation of degradation products reaches 15% the Dowtherm should be removed from the system and purified for operation at maximum temperatures. At the breakdown rate indicated in Table I, 15% concentration of undesirable materials would not accumulate until approximately the time indicated in Table II had elapsed.

TABLE II. PERIOD OF SERVICE TO BE EXPECTED FROM DOWTHERM AT VARIOUS TEMPERATURES, BEFORE PURIFICATION WILL BE DESIRABLE

Maximum Temperature in System	Time
650° F.	45—60 months
700	25—37
725	10—14
750	3— 4
775	1½— 2

The temperatures indicated in all cases in the above table are to be taken as the maximum temperature at any point in the Dowtherm system. The recommended maximum vapor temperature is 735 to 740° F. This means a top temperature of 750 to 760° at any point in the system.

Purification of Dowtherm

When it becomes necessary to purify the Dowtherm, owing to the accumulation of decomposition products, as will occur when operating above 700, two methods may be employed. These are, briefly, distillation and/or crystallization.

Where the available equipment is satisfactory, distillation is probably the more effective. The Dowtherm may be boiled in the regular Dowtherm boiler, the vapors passing up through the heat exchanger where they are condensed and may then be returned by gravity to a separate tank for cleaned, recovered material. If, when operating at a constant pressure, the temperature of the distilling vapors begins to rise, the desirable material has been recovered, and the distillation may be stopped and the residue discarded.

Purification by crystallization uses simpler equipment, but at the same time requires a little more handling of the material. The ma-

terial is drawn from the boiler into crystallizing pans which are suitably cooled below 54° F. This may require the use of circulating ice water. Crystals of Dowtherm appear around the sides of the container and a liquid residue remains. This may be separated from the crystals either by filtration, or preferably, be decantation, and the crystals may then be brought to room temperature and the liquid stored. The filtrate or supernatant liquid which contains the decomposition product may be put through another crystallization process, and this routine repeated several times until a product of satisfactory purity no longer separates, when the decomposition product will have been isolated and may be discarded.

Certain low boiling materials are formed in small amounts due to high temperature cracking of Dowtherm above 750° F. These include hydrogen and phenol and may be readily vented to the atmosphere.

Thermal Properties of Dowtherm

To make understandable the properties of Dowtherm, it is frequently desired to compare these properties with those of water. Table III makes these comparisons and Figs. 2 and 3 give additional data.

TABLE III. PHYSICAL PROPERTIES OF DOWTHERM COMPARED WITH WATER

	Water	Dowtherm A
Sp. Gr. at 212° F.	.9584	.9950
Relative Densities of Saturated Vapors not Corrected for Temp.:		
Ratio to Water at Atmospheric Pressure	1	7.5
Ratio to Water at 50# Abs. Pressure	1	8.95
Ratio to Water at 100# Abs. Pressure	1	7.3
Melting point, ° F.	32.0	53.6
Boiling point, ° F.	212.0	500
Specific heat of liquid at respective boiling points (B.T.U. per lb.)	1.005	.63
Heat of Vaporization at respective boiling points (B.T.U. per lb.)	970.2	123
Cubical Expansion coefficient (32-212° F.) Per ° F.	.00024	.00045
Abs. Viscosity of liquid at 212° F. (Centipoises)	.284	1.0

Table III shows that steam is nearly eight times as effective a heat carrier as Dowtherm at the boiling point. When it is remembered, however, that Dowtherm boils at nearly 500° and that the

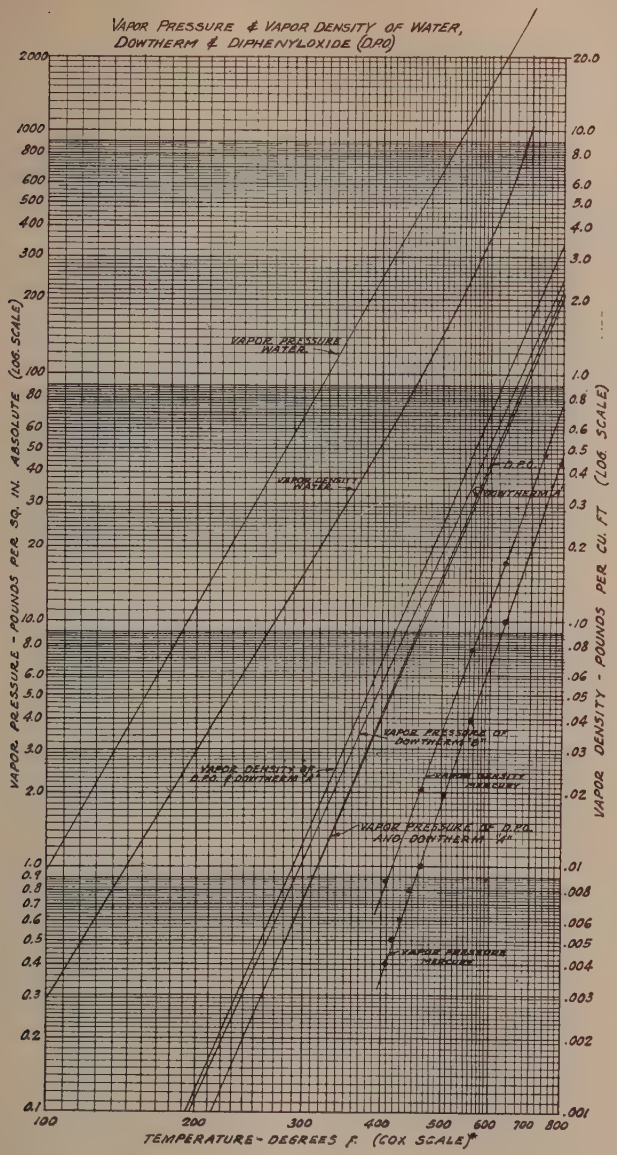
VAPOR PRESSURE & VAPOR DENSITY OF WATER, DOWTHERM & DIPHENYLOXIDE (D.P.O.)
VAPOR PRESSURE - POUNDS PER SQ. IN. ABSOLUTE (LOG. SCALE)
VAPOR DENSITY - POUNDS PER CU. FT (LOG. SCALE)
TEMPERATURE - DEGREES F. (COX SCALE)
VAPOR PRESSURE WATER
VAPOR DENSITY WATER
D.P.O. & DOWTHERM A
VAPOR PRESSURE OF DOWTHERM "B"
VAPOR DENSITY MERCURY
VAPOR DENSITY OF D.P.O. & DOWTHERM "A"
VAPOR PRESSURE OF D.P.O. AND DOWTHERM "A"
VAPOR PRESSURE MERCURY

FIG. 2. Vapor pressure and vapor density of Dowtherm, compared with water and with mercury.

pressure required to deliver steam at 500° will amount to several hundred pounds, the advantage of Dowtherm becomes more apparent. In view of its low specific heat, it can be shown that Dow-

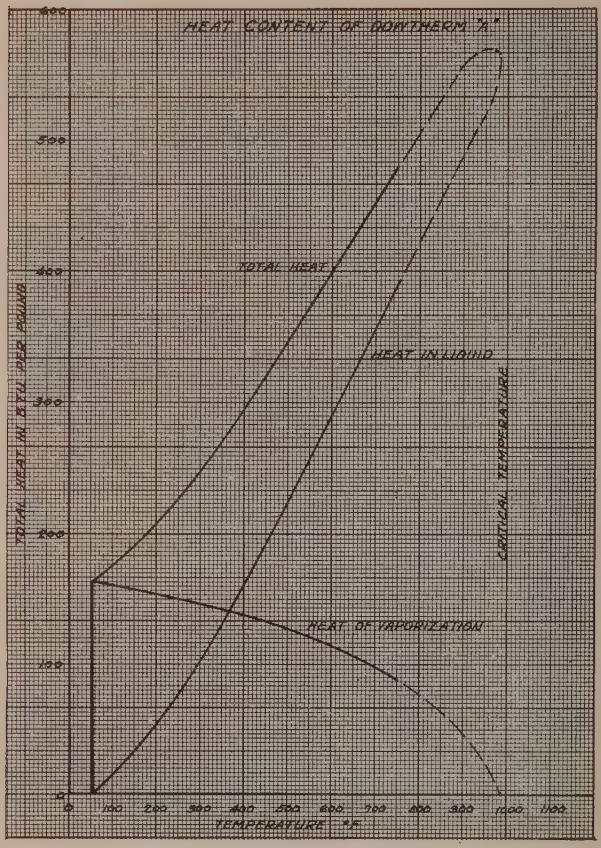

Fig. 3. Heat content of Dowtherm A.

therm can be brought up to its boiling point at a lower cost than that involved in bringing water to its much lower boiling point. The actual total heat in Dowtherm vapor at 500° is 345 B.T.U. per pound, while that of steam at 212° F. is 1150.4 B.T.U. per pound.

Dowtherm in the Generation of Power

A. Air Preheating [6, 7, 8, 10]:

The first large scale application of Dowtherm to production of power was in the plant of the Virginia Public Service Corporation in Bremo Bluff. In this plant the Dowtherm was used in an economizer in the stack, the heat absorbed in this economizer section being released in the air preheater. The air was heated both for combustion and for the mill drying of the pulverized fuel. The advantages which were originally claimed for Dowtherm in this particular application have been borne out in practice. The use of Dowtherm eliminates the large and ungainly air-ducts which so frequently clutter up the ordinary power plant. It also permits accurate and efficient control of air temperature separately for mill drying and for secondary air. The heat absorbing element located in the stack is constructed as an extended surface economizer. The absorbing element is placed directly over the top of the boiler, the flue gases passing vertically upward from the boiler through the heater to the induced draft fans at the base of the stack. The heat liberating elements are placed close to the mills and furnaces with which they are associated.

B. Steam Superheating and Reheating:

In the power plant of The Dow Chemical Company there is at the present time one large Dowtherm boiler.

In the first place, the boiler feed water must be completely deaerated and free from salts and other dissolved material. Water meeting these specifications is fed to the boiler at a pressure of approximately 1600 pounds per square inch. This boiler feed water is passed through an economizer located next to the stack and then into a series of coils in the water-wall furnace section. The boiler is not of the re-circulation type but is a single pass unit.

The water passes successively through an economizer, furnace coils and a convection pass and is released to steam into a superheater drum. See Fig. 4 and Table IV. The superheated steam is conducted directly to a turbine where it expands to 400 pounds pressure and approximately saturation temperature. It then goes to a reheater, where the temperature is again increased to 700°. From this point the steam is discharged to the plant 400 lb. superheated steam main, to be used in other turbine units.

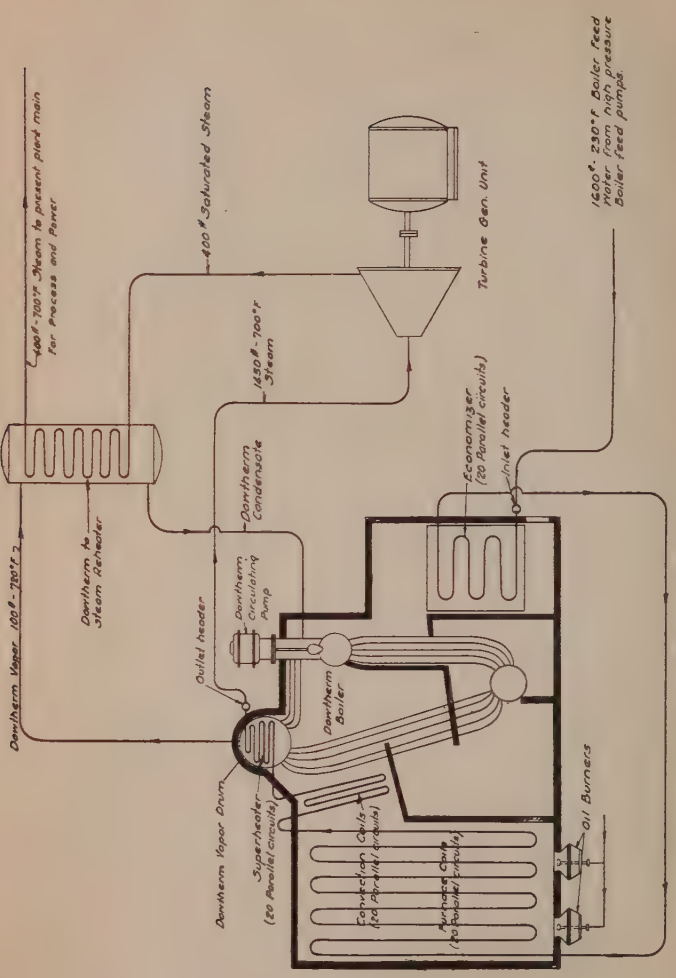
1400°-700°F Steam to present plant main for Process and Power
400 # Saturated Steam
Dowtherm Vapor 100°-750°F
Dowtherm to Steam Reheater
Dowtherm Condensate
1430°-700°F Steam
Turbine Gen. Unit
1400°, 230°F Boiler Feed Water from high pressure Boiler feed pumps
Economizer (20 Parallel circuits)
Inlet header
Outlet header
Dowtherm Circulating Pump
Dowtherm Boiler
Dowtherm Vapor Drum
Superheater (20 Parallel circuits)
Convection Coils (20 Parallel circuits)
Furnace Coils (20 Parallel circuits)
Oil Burners
FLOW DIAGRAM
1400 # SERIES TYPE STEAM BOILER UNIT USING DOWTHERM FOR INDIRECT SUPERHEATING AND REHEATING OF STEAM.

FIG. 4. Dowtherm boiler used in the exact control of superheat and reheat of steam.

So far we have not mentioned the manner in which Dowtherm is applied to this system. The superheater mentioned above really consists of the vapor drum of a separate boiler unit, through which Dowtherm is being circulated. The Dowtherm portion of the system is quite similar to an ordinary bent-tube boiler located in the path of the combustion gases between the water convection section and the water economizer. The Dowtherm is thus placed in circulation, and the vapors at 120 pounds pressure and approximateley 720° F. are released in the upper drum of the boiler. In this drum are placed the steam superheating coils heated by hot Dowtherm liquid and condensing vapor, and the steam temperature is raised from 585° to 700°. Dowtherm vapor is also carried from this drum through a single pipe to the reheater, where the exhaust steam from the turbine at 400 pounds pressure is reheated to approximately 700° F. This type of operation gives excellent control of superheat and reheat temperature, not otherwise possible. The Dowtherm condensate from the reheater is returned by gravity to the main boiler circulation. Circulation in the Dowtherm boiler is maintained by means of a propeller pump located in the upper rear drum, which forces the liquid downward through the rear bank of tubes. By virtue of the carefully planned arrangement of baffles in the boiler and of tubes in the economizer, the stack gases leave the system at reasonably low temperatures. It was originally intended to effect further economies by locating an air preheater beyond the economizer. This has not been done in the present unit because of the relatively low feed-water temperature.

When this unit was first placed in operation, the heat transfer in the steam reheater was calculated. The Dowtherm temperature was 713° F. The entering steam temperature was 476° and the exit steam 685°. At that time 100,000 pounds of steam per hour were being reheated. The reheater has an internal steam surface of 2950 square feet. From these figures, the coefficient of heat transfer in the reheater is 45 B.T.U./(sq. ft.)(hr.)(°F.). The reheater was not operating at maximum efficiency at the time, as it was planned for the reheating of 125,000 pounds steam per hour, at which rate the coefficient of heat transfer would have been 57 B.T.U./(sq. ft.)(hr.)(°F.). This is more nearly in line with what we would have expected from preliminary laboratory results, and this figure is now being approached in daily operation.

Under typical operating conditions the dry gas loss from the stack resulting from operation with only 10% excess air and combustion

of oil having a thermal value of 19,000 B.T.U. per pound, a 485° stack and 40° entering air, is approximately 8%. The hydrogen loss, based on 10½% hydrogen in oil and a temperature of 485° in the stack and 40° entering fuel, is 7½%. Radiation and unaccounted for losses—estimated at 3%, or a total loss of 18½%. The boiler efficiency, by difference, is 81½%. This compares very favorably with ordinary straight boiler operation, and when we consider the advantages of the Dowtherm boiler which operates at low pressure and which furnishes exact control of superheat and reheat temperature, the overall efficiency is very satisfactory.

TABLE IV. A TYPICAL OPERATING CONDITION IN DOWTHERM POWER PLANT

Steam generated per hour, based on boiler feed pump piston displacement	107,000 lbs.
Boiler feed pressure at the economizer entrance—	1600 lbs. per sq. in.
Steam pressure at the superheater outlet	1440 lbs. per sq. in.
Dowtherm pressure in the superheater drum	97 lbs. per sq. in.
Dowtherm temperature in superheater	695° F.
Steam pressure at reheater inlet	395 lbs. per sq. in.
Temperatures at various parts of the system are as follows:—	
Boiler feed water to the economizer	215-220°
Boiler feed water out of the economizer	360°
Water leaving furnace coils	590°
Steam leaving convection coils to superheater	605°
Superheated steam to turbine	685°
Steam to the reheater from turbine	467°
Steam out of the reheater	685°
Flue gas temperature—at the convection pass	1240°
at the boiler outlet	820°
at the economizer outlet or stack	485°
The turbine load varies slightly, but averages	1650 to 2000 K.W.

C. Heat Storage:

Another interesting but untried application of Dowtherm to power cycles is in its use as a heat storage medium.[9] Power plants are subject to varying loads, and they must of course supply the power as required. There is frequently a considerable expense for labor and stand-by losses to maintain additional boiler capacity in readiness for the increased load at the peak period.

To eliminate some of these operating difficulties and expenses,

furnaces and boiler installations have been devised capable of producing the maximum amount of energy which they will be called upon to supply, but usually operating on an average requirement basis. The excess heat which is generated during the off-peak period is absorbed in suitable equipment and is furnished in readily available form during the peak-load demand. Steam accumulators have long been used for relatively rapid fluctuations in the load, particularly in small power plants. They are not satisfactory for large power plants because such a system would call for high pressure equipment, which has not as yet proven economical.

A heat absorber similar to that used for air preheating [6, 7, 10] may be located in the stack to absorb excess heat from flue gases, transferring it into large storage tanks continuously at a slow rate and drawing on this heat reservoir to make steam or preheat the boiler feed water at times of demand. It may be argued that if Dowtherm is characterized by a low specific heat that it would be a poor heat storage medium. To overcome the deficiencies of Dowtherm as a storage medium, the following means have been proposed. The large heat storage tank may be filled with a heavy material such as scrap or pig iron bars or other heavy metal ingots. The heat which is absorbed by the Dowtherm from the flue gases would be transferred to this heavy heat storage material in the tank. The heat would not be removed from the tank until the boiler feed water or the steam for which the heat is intended is put into circulation in the heat exchangers. Such an accumulator and storage system has many advantages over systems now in use. In addition to the function of such a unit for heat storage for the preheating of boiler feed water, it would be possible to withdraw the hot Dowtherm from the tank, carrying it directly to an air preheater such as has been previously discussed. All of the heat obtained from such a storage system would be available at very low cost, since the heat which would be stored is now being lost through high temperature stack gases. At present the heat available in stack gases frequently exceeds the amount of heat required for preheating secondary air by as much as 30 to 50%.

Application of Dowtherm to Process Industry

Liquid vs. Vapor Heating

While a wide variety of applications of Dowtherm have been proposed for heating and cooling operations, there have been to date a

rather limited number of such applications in commercial operation. When Dowtherm is being considered as the means of conveying heat to or from an object, the first decision to be made is whether the transfer shall be effected by means of vapor or circulating liquid. In case of cooling operations, the liquid form will be simpler of operation and more efficient. An exception would be the rare case where it is desired, for example, to cool a reactor from 750° to 600° without the application of pressure. In such a case vapor of Dowtherm A at 500° can be used, but liquid Dowtherm C would be more desirable.

In heating operations it is usually necessary to have a temperature head of 30-50° when using the liquid and only 10-15° when Dowtherm vapor is used. At temperatures below 500° it is probably desirable to use Dowtherm in the liquid form, unless a constant subatmospheric pressure can be advantageously maintained in the system. When operating under a vacuum the same advantage of latent heat over sensible heat is obtained as at superatmospheric pressure.

As an example of the advantage of heating by means of condensing vapor as compared with circulating liquids, let us take a case where it is desired to transfer 50,000 B.T.U. per minute to the wall of the heat exchanger at 500° F. in a system in which the circulating pump has two inch inlet and outlet connections. The temperature should not fall below 500° F.

A. Liquid circulation, with a temperature head of 30°.

Heat in liquid at 530° F. = 240 B.T.U./lb.
Heat in liquid at 500° F. = 222 B.T.U./lb.
Difference, in dropping from 530-500° F. = 18 B.T.U./lb.
To transfer 50,000 B.T.U./min. requires 50,000/18 = 2777 lbs. = 390 gals./min.
Circulation is through 2" pipe, having capacity .174 gal./lin. ft., or 42.9 lin. ft./cu. ft.
Length of pipe to hold 390 gals. = 390/.174 = 2240 ft.
That is, circulation must be at the rate of 2240 ft. per min.
Circulation through pump = 2240/60 = 37.4 ft. per second.

B. Vapor Condensation:

Total heat at 515° F. = 352 B.T.U./lb.
Heat in liquid at 500° F. = 222 B.T.U./lb.
Difference = 130 B.T.U./lb.
To transfer 50,000 B.T.U. requires
50,000/130 = 384 lbs.
= 53.2 gals. liq. at 500°.

This is only 13.5% as much Dowtherm as needed in liquid form.

Feed to Dowtherm boiler in vapor system = 13.8% × 37.4 = 5.2 ft. per second.

In this case the temperature did not exceed 515° F. instead of 530° as in the first example. The demand on the pump is also much less strenuous.

Liquid Dowtherm as a Heating or Cooling Agent

Many of the products now being manufactured and having wide application to industry as a whole are solid at room temperatures. Such chemical materials must be manufactured and purified under conditions which do not permit of solidification in distilling apparatus. In such cases it is required to maintain the condenser at a temperature between the boiling point and the freezing point of the distillate so as not to permit its congealing in the condenser tubes. Dowtherm is being successfully applied to such an application in the manufacture of a product of this nature in our own plant. See Fig. 5. In this particular application the Dowtherm is heated with steam from nearby process equipment. It is then circulated through the tubular condenser at a temperature slightly in excess of the freezing point but considerably below the boiling point of the material being distilled. The down-leg from the condenser to the receiver is jacketed with a pipe through which Dowtherm is circulated so as to maintain the distillate in the liquid state until it is finally discharged to the reservoir.

The use of Dowtherm as a cooling agent is equally as important in many cases as its function as a heating material. It is much more successful as a cooling agent than the oils which have been used for this purpose, particularly in view of the fact that Dowtherm will not carbonize while circulating through the tubes in the heating or condensing portion of the reaction vessel.

An installation in which it is proposed to use Dowtherm as the cooling agent is of interest to those manufacturers who are troubled with exothermic reactions. In one such reaction it is desired to maintain the temperature at all times below 400° F. There is ordinarily a stage in the reaction at which a sudden evolution of heat occurs. At this stage it is desired to remove the excess heat by circulation of Dowtherm through coils immersed in the reaction vessel. The Dowtherm enters at approximately 200° F. and after leaving the reactor at 300° F, it is allowed to circulate through a pipe coil radiator

system which dissipates the heat to the atmosphere. The radiator may be of the fin type so that the system can operate on a minimum amount of the circulating liquid.

Dowtherm in Process Heating

As was indicated in earlier portions of this paper, one of the important applications of Dowtherm to industry is the heating of jacketed equipment which was constructed to withstand only certain low pressures. This type of equipment is very common in the chemical industry. Many units of this type are now being heated with Dowtherm vapors. Quite frequently such equipment is made to withstand a pressure in the neighborhood of from 35 to 65 pounds per square inch gauge. These pressures correspond to steam temperatures from 260 to 300° F. or they correspond to Dowtherm temperatures varying from 620 to 670° F. The general utility of such equipment is materially enhanced by the use of Dowtherm as a heating medium within its satisfactory pressure range.

Single Pass Boiler Unit for Industrial Dowtherm Heating

There is in the plant of The Dow Chemical Company one oil-fired, "straight-through" boiler unit for generating Dowtherm vapors which operates without preheated air and generates from 2,500,000 to 4,000,000 B.T.U. per hour.[14] This boiler operates at an over-all efficiency in the neighborhood of 60 to 65%. Dowtherm is entirely non-corrosive and may be used with any materials strong enough to stand the actual temperatures encountered. The furnace and boiler unit are constructed entirely of steel, there being no refractory material in the wall of the furnace itself. See Fig. 5. Forced circulation of the liquid Dowtherm permits location of the vapor-drum below the boiler, so that the entire boiler will drain back into it during the shut-down periods. The Dowtherm vapor is carried away from the drum at a pressure of 50 pounds, directly into the walls of the reactor and distilling unit which are being heated. The hot condensate from the jacketed still, which has acted in this case as a Dowtherm condenser, is returned to the expansion tank of the system through a heat exchange unit which serves to preheat the raw material being fed into the continuous still.

The boiler feed of Dowtherm liquid is maintained by means of a

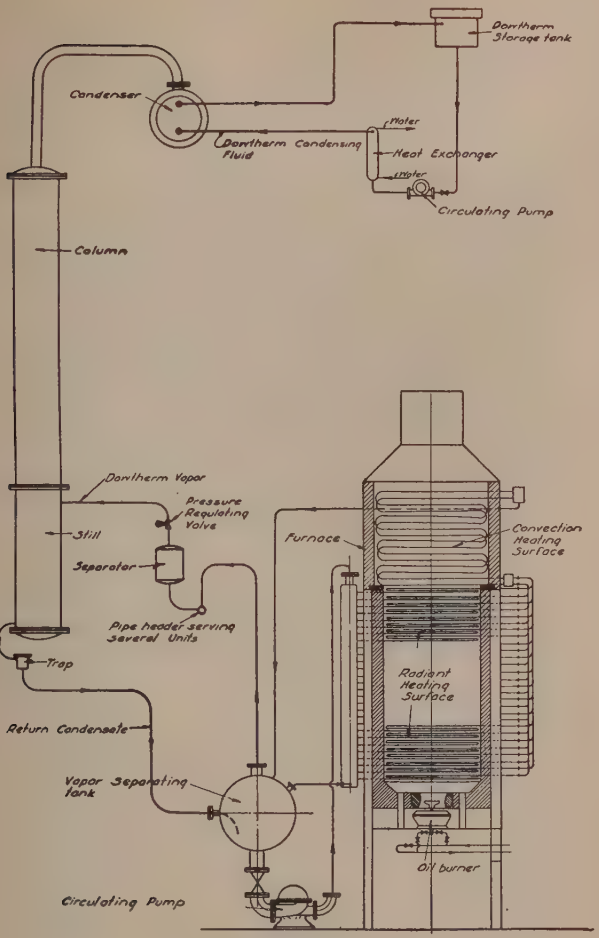

FIG. 5. Complete Dowtherm unit in actual commercial operation. This unit consists of separate boiler and condenser assemblies.

centrifugal circulating pump at a rate of 600 g.p.m. or approximately 3 feet per second. It is estimated that the Dowtherm vapor flashes out of the convection section at a rate of approximately 18 feet per second. The circulating pump has a cast steel casing and a forged nitrided steel shaft. It is good practice to use such equipment, as cast iron housings are frequently too porous. Likewise, cast iron moving parts do not stand up under temperatures such as are met in a Dowtherm vapor system. The Dowtherm circulating pump and the pump which feeds the fuel oil to the burner below the boiler are interlocked so that if for any reason the Dowtherm circulation stops the furnace will be shut down and overheating and decomposition of Dowtherm in the boiler unit are made practically impossible.

The customary precautions have been observed in selecting valves and fittings for operation at the temperatures prevalent in this unit. We have found that any valve which is satisfactory for operation with oil at given temperature will prove satisfactory with Dowtherm at the same temperature, providing that it has a deep stuffing gland. With reference to a level-gauge in the vapor separating drum and expansion tank, it has been discovered that the most satisfactory material is not the customary tubular sight glass, but is a flat sight-box of the type known commercially as Mica Sight. A Bristol type thermo-electric water column may also be used to indicate the liquid level. An ordinary pressure gauge is attached above the expansion tank. The only precaution which has been found necessary is that instead of using a curved or bent gauge-coil, a straight pipe connection is made from the tank to the gauge. This is to eliminate the possibility of Dowtherm condensing in the coils and blocking out the gauge from the system. The two 4-inch safety valves on the drum are set to open at 100 pounds pressure. As the normal operating pressure is only about 50 pounds, this setting insures that there will be practically no loss of Dowtherm through the safety valve. In addition, the fuel oil pump is provided with a pressure-actuated electrical cutout which shuts off the burner before the pressure reaches the setting of the safety valves.

Recirculation-Type Dowtherm Boiler

A similar installation is in satisfactory operation in another factory. This installation has been described as being particularly successful and is interesting since it operates at a higher temperature

than any other Dowtherm system in successful operation at the present time. The boiler to which we are now referring is a steel cased boiler of the forced flow recirculation type and supplying Dowtherm vapor at 144 pounds per square inch gauge pressure. This corresponds to a vapor temperature of nearly 760° and probably means that a temperature of 775° is attained in some of the radiant portions of the system.

The fact that these first two units in commercial operation in chemical plants for process heating were of the all-steel type does not need to indicate that a brick-set furnace would be impractical. There are commercially available brick-set furnaces with recirculation Dowtherm boilers of small capacities which are particularly adapted to small industrial applications. These are especially applicable where low head-room is available between the floor and the bottom of the vessel to be heated. This will frequently be the case, because in most cases where the equipment was primarily designed for operation with steam, no consideration was given to space from the floor to the bottom of the vessel. The construction of the building in which the equipment is placed will probably prohibit its being raised more than a few feet above the floor. In such cases brickset furnaces can be arranged to generate Dowtherm vapor for effective heating, and at a very economical figure.

In one plant a Scotch-Marine boiler with all welded joints is reported as in satisfactory operation in conjunction with a natural circulation Dowtherm Vapor system.

One application of Dowtherm, which is the subject of a British patent issued in 1930,[20] is in the processing of liquid hydrocarbons, particularly in the cracking of crude oil. The advantages claimed for this particular system are that the cracking is carried out under carefully controlled temperature and pressure conditions instead of in a direct fired furnace. This patent brings out one interesting point regarding the circulation of Dowtherm and the operation of the circulating pump. Since the pump may be working at high temperature, it has been found advisable to provide a cooling gland to the shaft driving the pump. This gland is said to be cooled by circulation of Dowtherm at a temperature of about 80° and at a pressure slightly higher than that in the Dowtherm system, so that any leaks through the pump are of cooled Dowtherm inward from the gland. This would seem to entirely eliminate the loss of hot Dowtherm outward from the gland, as occurs in many cases where an uncooled gland is

used. It has been our experience that the gland need not necessarily be cooled, but if a fairly tight-fitting steel shaft is used in a centrifugal pump and if a very deep stuffing box is added, that losses are reduced to a minimum. Where there are any losses from the circulating pump, these can be collected in a drip pan and occasionally poured back to the expansion tank in the system or returned by gravity to a sump or subsurface storage tank.

Additional Dowtherm Applications

Following are a number of different possible applications of Dowtherm to several process industries. These applications include domestic heating and cooking, which we must for the moment consider as being considerably in the future. Research on this problem is now in progress. Industrial heating of factories and buildings, the heating of jacketed reactors and kettles for candy making and for chemical reactions, evaporators, vacuum pans and crystallizing pans; the curing and vulcanizing of rubber, the heating and cooling of rolls such as used in the manufacture of glass, the heating of platen presses for moulded products; the heating of rubber moulds for vulcanizing and similar operations; the heating and cooling of soap reactors and for the production of hot water or steam. Dowtherm may be used for the melting of soft or hard solder. At higher temperatures Dowtherm may be used for the cracking and distillation of hydrocarbon oil.[20, 21] It may be used for melting zinc for hot dip galvanizing and the melting of type metal for linotypes. Tin-plating and similar operations can profit from Dowtherm applications. Lead-cable-sheath presses may be advantageously heated with Dowtherm.

Thermal Coefficients

The heat transfer coefficient from condensing Dowtherm vapors to dry steam was found to be in the range from 45 to 57 B.T.U./(sq. ft.)(hr.)(°F. total temp. dif.) in large scale operations. Dry gases are poor heat carriers, as are viscous liquids. These figures agree very favorably with data published by McCabe on the transfer from condensing diphenyl vapors to asphalt through the walls of standard 1 inch pipe.[11]

The film coefficient of Dowtherm A has been found to be in the range between 230 and 380 B.T.U./(sq. ft.)(hr.)(°F. total temp. dif.) at Dowtherm velocities from 5 to 9 feet per second.

In one large scale experimental unit where it was desired rapidly to cool the Dowtherm vapor and effect its condensation before returning the material to a heat absorber, the vapor was passed through a condenser which was cooled by water at or near room temperature. The Dowtherm vapor entered the condenser at a temperature of 600° and left at a temperature near 300° in the form of liquid condensate. The over-all transfer coefficient from condensing vapor to water in this case was found to be 75 B.T.U./(sq. ft.)(hr.)(°F.). In another case Dowtherm vapor was used to pre-heat an organic compound prior to distillation. The organic material entered the preheater at a temperature of approximately 300° F. and was heated by Dowtherm vapor which entered the heat exchanger at 600° and left at 580°. The coefficient of heat transfer from condensing vapor to the organic liquid was 62 B.T.U./(sq. ft.)(hr.)(°F.). These results, though meager, should be of assistance in estimating the Dowtherm requirements in a given application.

Conclusion

We have attempted to correlate much of the previously published data on Dowtherm and to add other interesting and important facts regarding this fluid. The descriptions of a Dowtherm system for power generation, and various industrial applications of Dowtherm have been included to suggest possible uses for high-boiling heat transfer media in the reader's own field of activity.

We have tried to show the existence of a definite place for Dowtherm as a heating agent in the range 450-750° F. Our experience leads us to expect overall heat transfer coefficients from Dowtherm vapor to steam or to various organic compounds in the range 45 to 90 B.T.U./(sq. ft.)(hr.)(°F. total temp. dif.).

We have not indicated sources of commercial equipment for the generation of Dowtherm vapors because all of the leading boiler manufacturers are in position to install units for this purpose.

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Discussion

Chairman Marshal. : Mr. Heindel's paper is now open for discussion.

C. Iddings: Mr. Chairman as I arrived in a little late it is possible Mr. Heindel may have covered the point I have in mind. In practice, was there any tendency for these mixtures to separate, that is one compound to separate from the mixture, especially, when going through the vapor phase?

R. L. Heindel: If you will recall, the mixture which we considered chiefly was the one we called Dowtherm "A," which is a mixture of diphenyloxide and diphenyl, the boiling points of which vary only five degrees. That is, diphenyl boils at 491 degrees F. and diphenyloxide at 496 degrees F., in the pure state. The technical grades of these materials have boiling points very close together so that separation is not an important consideration.

C. Iddings: Does that also hold for the other mixtures.

R. L. Heindel: It is desirable, of course, in preparing mixtures, to have the boiling points as close as possible. The naphthalene mixtures has not proved as satisfactory as the diphenyl mixture because of that difficulty, and also because of the fact that it has a narrower range of application, its boiling point being somewhat lower than that of the diphenyl mixture.

M. J. Kermer: What kind of materials can be used in the construction and fabrication of the boilers and the various apparatus. Is it possible to weld to a joint and if so, what materials are used.

R. L. Heindel: Thank you for bringing up that point, which I should have mentioned. Any material of construction will prove satisfactory that has sufficient strength to stand the actual temperatures involved. Pressure is no consideration because we operate at very low pressure. At 750 degrees F., for example, the gauge pressure on the system is only in the neighborhood of 150 lbs. The customary construction utilizes ordinary boiler plate, black iron pipe and the customary type of oil valves and fittings. It is not desirable to use cast iron at these high temperatures because of the porosity of the cast iron.

W. I. Burt: It is often necessary to have stuffing boxes on pumps. I have trouble in packing these stuffing boxes. Is there anything you can recommend to hold it

R. L. Heindel: In general, the recommendation is that the stuffing boxes be made as deep as possible. The packing which we have found to be quite satisfactory is a heavily graphited material. I think the packing is asbestos in nature and heavily graphited. I can give you the trade name if you will see me after the session.

Chairman Marshall: If there is no further discussion we will proceed to the second paper on this morning's program: "Mercury Vapor as Applied to Process Industries," by Mr. Charles A. Hulsart, of the Babcock and Wilcox Company.

MERCURY VAPOR AS APPLIED TO PROCESS INDUSTRIES

By CHAS. A. HULSART *

The use of mercury vapor as a medium for the transfer of heat is neither new nor untried. The first commercial applications to chemical processes, so far as we know, were made in 1915, in connection with the distillation of beta naphthol and the sulphonation of naphthalene. Since that time there have been installed nineteen, or more, mercury units, of which the best known are those being used by the Sun Oil Company, Philadelphia, Pa., for the distillation of lubricating oils. Along with the investigation and development of mercury vapor as applied to chemical processes, considerable advances were made in the field of power generation, until today there are three large mercury-steam-electric units in commercial use.

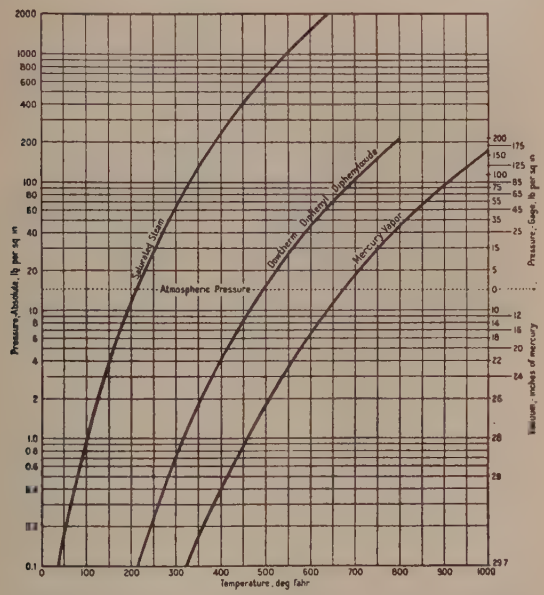
This gives assurance that the pioneer period of development in the use of mercury vapor is past—that we have reached that point where sufficient knowledge and experience are available to assure the utilization of mercury vapor on a sound engineering basis, either in the fields of power generation or of process heating.

The advantages of saturated vapors over direct flame, hot-liquids, or hot-gas methods of heating is evidenced by the general use of saturated vapors when the temperature range is within their limits. Engineers have long appreciated the fact that in the vapor stage the temperature of a saturated vapor medium remains constant and only the latent heat of the vapor is utilized in the heating or cooling process. With mercury vapor added to this class of heat-transfer media, the temperature range of vapor heating is materially increased. As a matter of fact, the only temperature limitation of mercury, insofar as the heating medium is concerned, is the upper temperature limit of the metals used for heat-transfer equipment.

The respective temperature pressure ranges of the three principal liquids used for vapor generation—water, the diphenyl liquid group, and mercury—are illustrated by the curves shown in Fig. 1.

* The Babcock & Wilcox Co., New York City, N. Y.

Assuming six pounds absolute as the minimum practical operating pressure for all three liquids, there is a temperature range for steam from 170 degrees Fahrenheit at six pounds to 636 degrees Fahrenheit at 2000 pounds; for the diphenyl liquids from 425 degrees Fahrenheit at six pounds to 735 degrees Fahrenheit at 136 pounds, and, for mercury, from 591 degrees Fahrenheit at six pounds to 1000



Graph showing pressure-temperature relations of saturated steam, phenolic liquids and mercury vapor

Fig. 1

degrees Fahrenheit at 180 pounds. However, with the mercury vapor process, by use of the "puff" system, the lower limit of temperature may be reduced to somewhat less than 350 degrees Fahrenheit. Mercury is used in the lower limits only in cases where exact control of temperatures and simplicity of equipment are essential, as these temperatures are within the temperature range of either steam or the diphenyl liquids.

Mercury has in its favor, as a medium of heat transfer, the following particular advantages over other liquids—

1. The required temperature is obtained with a considerably lower pressure.

2. It is an element and, therefore, has no tendency to dissociate or form compounds by rearrangement of its atoms.

3. It is not a solvent for, neither does it form amalgams with steel. There is, therefore, no tendency to foul the heating surfaces, nor to change the quality or quantity of the heat-transfer medium in the system.

It does have, in both the liquid and vapor states, a scrubbing action on the steel surfaces and, although all surfaces coming in contact with mercury should be sand blasted or pickled before assembly of the unit, the mercury will find and clean off all particles of mill or welding scale and any other foreign matter which might be present. This requires that provision be made, in the design of the apparatus, for removing this material until such time as the system is clean. This will be accomplished in several weeks of operation, after which the system may be sealed and operated over long periods.

4. Mercury solidifies at minus 38 degrees Fahrenheit, which, for all practical purposes, eliminates the freezing hazard.

5. The high specific gravity of the liquid makes it possible to return condensate to the boiler by gravity, with the head-room available in most of the existing process buildings, thus eliminating the necessity for pumping equipment of any kind.

6. Mercury and its vapor are non-inflammable, and is, therefore, practically suited to chemical processes in which the material being heated is combustible or explosive in the presence of flame.

Other advantages include: low cost of attendance, low maintenance, and the small space required for installation. Any source of heat can be used with mercury systems, such as oil, gas, coal, or electricity.

It is not the intent, of the foregoing, to give the impression that the mercury process is the magic wand of heat transfer work, or that it is so far superior to other methods that it alone should be considered, for such is not the case. There are, and will continue to be, many cases of application where other liquids are more economical and the question as to which medium is the most economical should be decided on its merits after all engineering and economic factors have been given due consideration.

An erroneous impression prevails so generally regarding the

dangers of mercury poisoning that it is desirable to state, briefly, the facts of the matter at this point, because the question is so frequently raised, even by chemical engineers. This impression arises, we believe, because of the general misunderstanding of just what constitutes mercury poisoning. Also in the early stages of the use of mercury, considerable difficulty was experienced in handling it, with the attendant danger of mercurial poisoning. The Babcock & Wilcox Company gave this question very serious consideration when it first commenced its extensive work on mercury boilers, about 1924.

At that time, an exhaustive investigation into this subject was made. Leading authorities in the medical and manufacturing fields were consulted and the experience of the General Electric Company with mercury over a period of several years prior to that time was taken into account.

This investigation proved conclusively that there is no need to fear mercury poisoning, in fact in all of the experimental work carried on by the General Electric and The Babcock & Wilcox Companies with mercury vapor apparatus no one engaged in this work has experienced even a moderate case of poisoning.

It is commonly believed that mercury vapor is colorless, odorless and tasteless, and while this may be strictly true of the vapor in very minute quantities, such as would be given off by ordinary evaporation from a container standing in a room, a vapor leak from a system under pressure is readily visible in the form of a dense gray cloud attended by a silvery deposit caused by condensation on adjacent cool structures. Anyone exposed to such a leak is decidedly aware, almost immediately, of a brassy taste in the mouth and discomfort in the throat.

Such a leak will, of course, occur only in systems operating above atmospheric pressure. In a great many industrial heat-transfer units, the mercury vapor will be used at pressures less than atmospheric. Any leak, therefore, would be of air into the system, rather than of mercury vapor, outward.

It must be remembered that in many industrial plants the operators are accustomed to handling freely poisons, that are considerably more dangerous than mercury or mercury vapor. Mercury vapor, if in sufficient volume to cause serious effects, produces so much discomfort in the person exposed to it that he has ample warning of its presence. If the mercury vapor is not in sufficient volume to be tasted, seen or smelled, it soon produces a severe headache and thus gives

ample warning that it is present. If exposure is continued, the headache is followed by distress in the alimentary canal, such as an extreme looseness or constipation; if either of these distresses are experienced, the person would, in a properly operated plant, seek immediate relief.

In central stations, the maximum precautionary measures are taken, but these, at the most, are really the simple principles of hygiene, most of which should be practiced even if there were no mercury in the vicinity. As a matter of fact, the physical condition of operators of mercury equipment has actually been found to be considerably above that of the average operator, because of the habits of cleanliness insisted upon by the employer.

In general, the following simple precautions are observed in central stations where large volumes of mercury are used:

1. Men are given a medical examination prior to being associated with mercury; those susceptible are thus eliminated at the start. Frequent examinations of operators are made, to keep a check on their condition.

2. Operators bathe and change clothing completely before leaving the plant. Work clothes and street clothes are kept separate. Clean work clothes are provided.

3. No smoking is allowed in the boiler room, and tobacco is used elsewhere only after the face and hands have been washed.

4. No food is kept or eaten in the boiler room. Before eating workmen wash their face and hands and brush their teeth.

5. Potassium chlorate mouth-wash is provided.

6. Boiler room, turbine room, etc., are kept scrupulously clean and well ventilated.

7. When handling liquid mercury, rubber gloves are worn under the regular work gloves.

8. Blower-type masks are provided for use when working inside any apparatus.

In this connection, it will be of interest to note that a mercury detector has been developed to a high state by the General Electric Company that will take continuous samples of flue gases or air in the room and which is sensitive to one part of mercury in several millions.

The equipment for process heating by mercury vapor may be divided into classes consisting of:

1. In which the vapor temperature is obtained at pressures below atmospheric pressure.

2. In which the temperature is in a range of pressures from atmospheric pressure up to approximately 30 lb. gauge.

3. In which the temperature is above approximately 30 lb. gauge.

Each of these three classes require a separate method of control.

In class No. 1, the control is provided by utilizing air at atmospheric pressure and vacuum to control the passage of mercury vapor

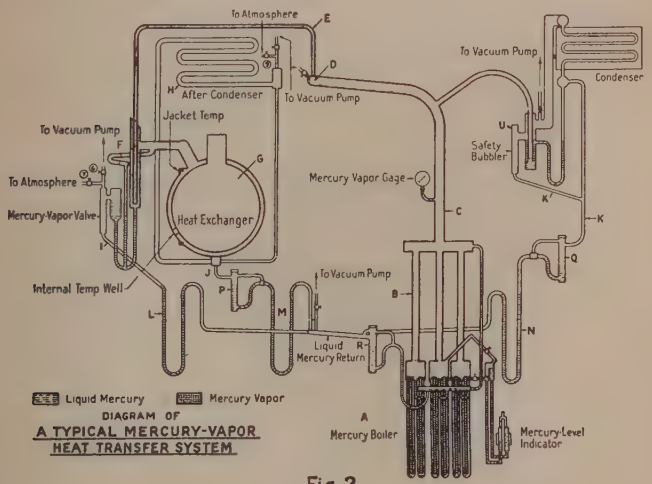


Fig.2

to the heat exchanger. In class No. 2, the temperature is controlled by providing an artificial atmospheric pressure, the use of which, with vacuum, controls the passage of mercury vapor to the heat exchanger. Class No. 3 is simply the conventional type of control for pressure vapor heating.

The application of Class No. 2 is limited by the cost of the liquid mercury in the barometric leg of the mercury vapor control valve only.

A typical installation of mercury vapor heating as for Class No. 1 is shown by Fig. 2.

It will be noted in this figure that A is the mercury boiler, in which the headers from the sections of the boiler are joined together by connecting tubes B in a single main header C, which branches off at D into a number of service headers, one of which is indicated by E. Each of these is connected through the valve F to a heat absorb-

ing or mercury vapor condensing unit G. Vapor after-condenser H is provided, connected as shown. Return lines I, J, and K, from the mercury vapor valve, the roaster, and the safety bubbler, lead to traps L, M, and N, and cleanouts P, Q, and R.

The safety bubbler U is merely a safety valve, and differs from the ordinary steam safety valve in that it does not open to the atmosphere, but opens instead, into a closed condenser, with provision for returning the condensate back to the boiler by gravity. It also differs from the usual steam safety valve in that the specific gravity of the liquid is so great that no mechanical parts, such as valve springs or valve seats, are necessary, a barometric leg of liquid mercury replacing the valve seat and disc of the conventional type of safety valve.

The control of the temperature in the heat exchanger is accomplished through the mercury vapor control valve, the purpose of which is three-fold: First, to permit shutting off the mercury at will from the heat exchanger, and to permit the entrance of the mercury vapor whenever desired; second, to permit the operation of the heat exchanger at a low pressure without endangering the operation of the boiler, and, third, to control the mercury vapor without in any way presenting a metallic surface other than liquid mercury as a valve seat.

The mercury vapor control valve is operated by the difference in pressure between the atmosphere and the lesser pressure within the unit; that is, the column of liquid mercury in the mercury control valve is regulated by raising and lowering the mercury level by intermittent exposures to atmospheric pressure. By the raising and lowering of the level of the liquid, the supply line through which the mercury vapor is passed to the heat exchanger, is opened and closed; in other words, the liquid mercury when raised in the valve submerges the inlet end of the vapor supply pipe in liquid mercury, thus preventing the passage of mercury vapor from the supply line of the boiler to the supply line of the heat exchanger.

By this method of control, there are none of the usual conventional types of valves exposed to mercury, and, consequently, there is no maintenance of valves or valve seats.

A further unique feature of this system is the possibility of operation of the boiler at a comparatively high mercury vapor pressure on the heat exchanger in such manner that during the heating-up period the full benefit of this higher pressure is obtained in the jacket of the heat exchanger, so as to cause quick heating,

and, following that, the maintenance of the required temperature in the heat exchanger, corresponding to a very much lower mercury vapor pressure by what may be termed the "puff" system. In this method, the valve is alternately opened and closed, to permit the injection of a small quantity of mercury vapor at higher pressure at each operation. This mercury vapor expands suddenly, producing the low pressures and low temperatures required in the heat exchanger.

Briefly, the operation of the "puff" system is accomplished through manipulation of valve No. 7 (to atmosphere) and valve No. 6 (to vacuum). Assuming the unit on the line and mercury vapor passing to the heat exchanger, and the temperature approaching the upper limit, valve No. 6 in this case being open and valve No. 7, to the atmosphere, being closed, thus putting a vacuum on the reservoir side of the mercury vapor control valve.

To stop the flow of mercury vapor to the heat exchanger, valve No. 6 to the vacuum pump is closed, and valve No. 7 to the atmosphere is opened. The in-rushing air at atmospheric pressure replaces the vacuum, which drops the liquid mercury in the reservoir, and this liquid mercury then flows into the lower chamber of the vapor valve, submerging the lower end of the vapor supply pipe in liquid mercury and thus stopping the flow of vapor to the heat exchanger.

As the heat in the mercury vapor surrounding the heat exchanger is absorbed, the temperature will drop, and, when the temperature reaches the lower temperature range of operation, the passage of more vapor mercury to the heat exchanger is accomplished by closing valve No. 7 to the atmosphere and opening valve No. 6 to the vacuum. This evacuates the air on the reservoir side of the valve, thus withdrawing the liquid mercury from the vapor side of the valve, and exposing the lower end of the vapor pipe to the source of mercury vapor, and mercury vapor again flows to the heat exchanger.

In the foregoing description of the operation of the unit, it might be assumed that the valves No. 6 and No. 7 were hand operated, whereas, in actual service, this is accomplished by automatic controls, which operate on temperature, and these controls may be made by either regulating the flow of mercury vapor by the temperature of the material in the heat exchanger or by the temperature of the mercury vapor surrounding the vessel.

In addition to the automatic controls for the passage of vapor to the vessel, there is usually provided an automatic control for the fuel burner. This control operates from the pressure or temperature

of the mercury vapor in the vapor main adjacent to the boiler, which automatically controls the amount of fuel burned in accordance with the requirements of the heat exchanging equipment.

Fig. 2 shows but one heat exchanger, for purposes of illustration, but multiples of heat exchangers may be taken from the same vapor main. Each heat exchanging unit would be complete with its own mercury control valve, after-condenser and automatic controls.

The after-condenser performs several functions.

1. With the "puff" system, the after-condenser provides an additional amount of heating surface available in order that the temperature in the mercury vapor heating element may be uniformly distributed. It will be found in practice that the mercury vapor will actually rise to a given point in the after-condenser, and this point may frequently be used, in lieu of a thermometer, to ascertain the operating temperature inside the heat exchanger.

2. The second important function of the after-condenser is to collect the air remaining in the system after evacution and to vent it. Before placing the unit into operation, it is evacuated to approximately .2 millimeter upon starting, but, due to the high temperature of the mercury vapor even this small amount of gas remaining after evacution rises to a considerable vapor pressure relative to low pressure of the mercury vapor, and may produce difficulty if some provision is not made for collecting this remaining gas.

3. The third function of the after-condenser is to act as a protector to the vacuum pump, in order that under no conditions mercury vapor can be carried to the vacuum pump, even though the heating surface of the heat exchanger is completely bathed in the mercury vapor.

On the lower end of the after-condenser there is installed a manually-operated valve No. 9, to the atmosphere. This valve is for emergency use, in the event that for any reason it is desired to eliminate the mercury vapor in the heat exchanger. This is accomplished by opening the valve which permits air to enter and displace the vacuum, thus causing rapid condensation of the mercury vapor and stopping the boiling of the liquid mercury in the system. This, of course, is only for emergency operation, as it is important that as little air as possible should enter the system, as oxygen combines with both mercury and steel to form oxides that would have a tendency to foul the system.

The returns for the liquid mercury are equipped with traps and sumps. The sumps permit the removal of mill scale and sludge, that are carried through the system in suspension, and should be cleaned out frequently, when the equipment is first put into operation; it will be found, however, that the amount of mill scale and other foreign material obtainable from the sumps will diminish to the minimum

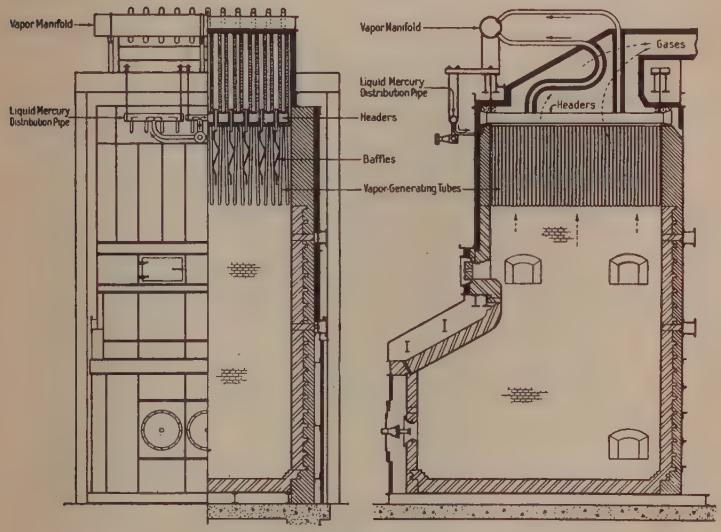


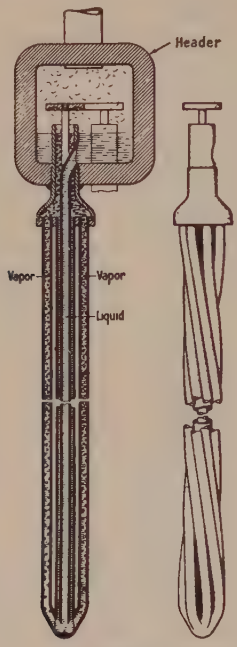
Fig. 3 Sketch of Typical B. & W. Mercury Boiler

within a few weeks, after which the necessity for further cleaning will be infrequent.

The design and operation of mercury vapor equipment for the second class, where an artificial atmosphere at about 30 lb. is provided to replace air at atmospheric pressure, is similar to that described for class 1, and for the third class, where the temperature range is over 30 lb. gauge, the design and operation of the unit is similar to either steam or high-boiling-point liquid systems other than mercury; that is, the unit is designed to work at a positive pressure, and control is maintained through valves and the safety valve exhausts taken care of through safety valves of the conventional design but modified, as necessary, for mercury vapor service. In addition, because of the value of the mercury, closed-condensing equipment is provided on the

safety valve exhaust to conserve the mercury passing through the safety valve exhaust.

Due to the high specific gravity of liquid mercury, and due, also, to the fact that liquid mercury does not ordinarily wet steel, it is necessary to provide a boiler of special design for this service.



B&W Mercury-Vapor Generating Tube
Fig. 4

There have been certain theories on using other metals, such as sodium, for forming an alloy with liquid mercury for the purpose of wetting the surfaces in the boiler, and thereby obtaining higher rates of heat transfer.

A typical mercury boiler is indicated by Fig. 3, and consists of horizontal headers into which are inserted mercury vapor-generating elements. These elements extend downward into the hot gases of the furnace, and each contains its own system of circulation.

The design of the mercury-vapor-generating tubes is shown in Fig. 4.

In the design of a mercury vapor heating unit, all material that comes in contact with mercury must be made of steel, or, for extremely high temperatures, special steel alloy, for the reason that, of all our structural metals, steel, alone, is not subject to attack by mercury, except in very insignificant degree.

The question as to whether or not mercury wets the surfaces of a mercury boiler is somewhat controversial. It is known that if steel is cut in a bath of liquid mercury, the surfaces will be wetted. However, as it is impracticable to manufacture commercial equipment by any such method, all design is on the assumption that the mercury does not wet the surfaces of steel, and all formulas for heat transfer have been based on this principle and checked by actual tests.

The cost of the liquid mercury is often raised as an argument against its use. This is not justified, for the reasons, first, that the amount of liquid mercury required is small; second, that there is practically zero deterioration, and third, that mercury is always resaleable at practically the market price, which means that the only loss chargeable to the use of liquid mercury in a system is the interest charge on its initial cost.

In addition to the use of mercury vapor in the transfer of heat to process material, mercury has also been used as a cooling medium for exothermic reactions, as well as in a combination requiring, first, heating, and then cooling. The cooling is accomplished by providing in the heat exchanger a reservoir of liquid mercury, so that, when the temperature of the material reaches its maximum, and it is desired to cool it, the mercury vapor is shut off and the liquid mercury allowed to boil, and thus absorb either the residual heat or the heat caused by chemical reaction, the mercury vapor being condensed and returned to the boiler by gravity or returned to the heat exchanger for further cooling.

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Discussion

Chairman Marshall: Mr. Hulsart's paper is now open for discussion.

I. L. Newell (written): The paper by Mr. Hulsart is an excellent one from a chemical engineering standpoint. However, the references to the toxicity of mercury might prove somewhat misleading to those not entirely familiar with metallic poisons. In view of the lack of quantitative data in Mr. Hulsart's paper on the amounts of mercury vapor necessary to cause poisoning, the following figures taken from published data may be of value.

International Critical Tables states that a concentration of less than 0.000125% (10.3 milligram per cubic meter) mercury vapor causes symptoms of poisoning after daily exposure for two or three months.

Henderson and Haggard in their monograph, "Noxious Gases," state that the inhalation of 0.4 to 1.0 milligram of mercury vapor daily causes poisoning after some months, and that poisoning results after two or three months from the inhalation of air containing 0.0007 milligram of mercury per liter (0.7 milligram per cubic meter), when the exposure is three to five hours daily. The total daily absorption under these circumstances was estimated as between 0.771 and 1.285 milligrams.

A recent study on the toxic concentration of Mercury by Fraser, Melville and Stehle (Journal of Industrial Hygiene, March, 1934) shows that the toxic effects resulting from the continued inhalation of mercury vapor may be acute, subacute, or chronic (fatal or non-fatal), depending upon the concentration of the vapor inhaled. A concentration of 1.89 milligrams of mercury vapor per cubic meter of air, inhaled 8 hours daily during a period of 40 days did not produce any ostensible evidence of mercury poisoning. The minimal concentration of vapor which lead invariably to chronic toxic effects under similar conditions of exposure was 3.05 milligrams per cubic meter.

The fact that mercury can evaporate at low temperatures is often responsible for cases of poisoning. At a temperature of 20° C. a cubic meter of air can hold as much as 15.2 milligrams of mercury vapor, while at 30° C., 33.9 milligrams can be held.

In my opinion the experience of the General Electric and The Babcock and Wilcox Companies with mercury vapor apparatus and no attendant cases of mercury poisoning is not due to a non-toxic property of mercury vapor, but due instead to the high quality of engineering and construction of the mercury vapor equipment, and precautions observed where mercury is used. In addition to the safeguards mentioned by Mr. Hulsart when large volumes of mercury are used, I believe that periodic examinations of the atmosphere in which the operators work would be an additional safeguard well worth the time and expense involved.

MR. MCKEEN: I think the author may have had a tendency to over-emphasize the poisoning hazards of mercury in the paper. I say this for two reasons, first because I have operated a system very similar to the case illustrated on the slide, and have found no cases of mercury poisoning at all, in fact, no indication of mercury poisoning. The precautions that he outlined were not even observed in any way and, as I say, the operators were inspected occasionally and found to be in perfect health. And, second, because I have supervised the manufacture of various mercurial salts and know very well the hazards that are to be encountered.

In connection with the "puff system" as applicable to this type of process heating, I might say that we have operated our mercury boilers obtaining temperatures as low as 250 degrees Fahrenheit and up to around 750 degrees Fahrenheit, having in mind the fact that the installation was designed to operate as a vacuum system.

I might add also that we have found the system exceptionally reliable. We have operated it twenty-four hours a day for about two years and have never had any difficulties in getting the desired B. t. u. efficiency required, that is, a million and a half B. t. u.'s per hour. We were able to take ordinary laborers and train them to operate this system within a period of two or three days. Of course that is exceptionally important now under the NRA conditions, where we must have three different men operating an apparatus such as this.

C. A. HULSART: On the question of mercury poisoning, we find ourselves in a position a good deal like your medical doctor. You go to your doctor and ask him what is wrong with you and he finds quite a little and he suggests that you go to Bermuda and that you stay away from work, also that you take plenty of outdoor exercise and a lot of other things that only a millionaire can do and you just simply cannot do them and you do not do them and neither do you die. Well, the manufacturer of mercury equipment is pretty near in the same position as the medical doctor. He tells you just what you should do, and he knows very well that you are not going to pay any attention to what he says.

H. K. MOORE: I notice that you speak of its non-effect on steel. Now, many of us know that steel, in many places, cannot be used

and I would like to know what is the effect of the mercury vapor on nickel.

C. A. HULSART: It just will not work. But, so far as nickel is concerned, we have today ni-clad steel, and we can manufacture steel with the nickel on one side of it to go against the material in your heat exchanger and on the other side we have the steel which takes the mercury vapor. We have also perfected a way of performing that process in ni-clad steel tubes, with either the nickel on the inside or the nickel on the outside and also we have our technique on welding up to such a point that we can make our joints between the ni-clad material with the nickel welding on the nickel side and steel welding on the steel side.

H. K. MOORE: You say you can put the nickel on the inside of the tube?

C. A. HULSART: Yes.

H. K. MOORE: Well, that is the important point I had in mind. That's just what I wanted to know.

M. H. ITTNER: Mr. Moore's question was whether nickel would work. Now I would like to carry that question just a little bit further. Does it work in these chrome-nickel steels where there is only a small amount of nickel present?

C. A. HULSART: Yes, we have used chrome-nickel steels very successfully for mercury boiler construction.

G. N. HARCOURT: In 1916 I had the pleasure of working with Mr. Field on a mercury application for the one Mr. Hulsart mentioned. At that time we were able to obtain a distillation of betanaphthol free from alphanaphthol, and we produced exceptionally pure betanaphthol at that time.

Later, I was associated with Mr. Downs in the installation of mercury heaters, mercury converters, for the catalytic oxidation of naphthalene. At those times we had a great deal of difficulty with the materials of construction. Welding was about the only thing that we could use; you cannot use any sort of riveted joint in a thing of that kind, and your welds must be absolutely free of any inclusion of iron oxide. Mr. Hulsart's company has, I believe, developed that technique of welding to the nth degree, and we are able to obtain mercury boilers now which are absolutely dead tight. They can be put under vacuum and left that way for twenty-four hours with practically no drop in vacuum. That is a very essential thing in working with mercury because it is obvious that you cannot have infiltration of air which might unite with the mercury forming solid oxides, which have to be removed in those takeouts and cleanouts that Mr. Hulsart showed on his sketch. I would like to say a few words about the "puff system," which has been developed to take care of different rates of heat input. You will very often obtain or have a piece of chemical equipment which you have to heat up very rapidly, have to heat the contents, the container, and its insulation on all the sur-

rounding piping and everything of that sort, and drive off moisture. During that period you will want a very high heat input. That can be obtained by operating at the high range of pressure for the installation which might be, as Mr. Hulsart said, six pounds. Then you come to the point where you wish to perform your reaction at a certain temperature. Then you have to hold the temperature at a given point for a period of three hours, more or less, and during that time the only heat that you have to supply is that due to radiation, and with a mercury system of this kind, using the puff system, you can obtain a terrific input during the time that you want it and then just enough heat to make up radiation during the remainder of the time.

CROSBY FIELD: I think we ought to realize that Mr. Hulsart's paper marks a very definite point in the development of mercury vapor heating, cooling and temperature control. The first thing you have to do, in the application of any new process before you can really make it a commercial every day proposition, is to have the three essentials—methods, materials and men. The methods have been with us for many years. The materials we have had over a decade of development, followed by another decade of actual every-day commercial use. We now also have the men, from engineer to construction man, experienced in the design, construction and operation of all types of mercury vapor installations. The combination of methods, materials and men, when grouped together in one organization or group of organizations, gives us that organized experience which takes a thing out of the laboratory stage and puts it into real commercial practice. That is what has happened to mercury as of this date. Sometimes that experience goes out into many other groups than that inherent in the method itself. For example, this development of materials has taken in all lines, including such things as X-ray work, metallurgical work, both ferrous and non-ferrous, and so on.

When it came to developing this puff system, for example, I happened to have the very great cooperation of the makers of temperature control units, showing how wide a separation there is between ordinary temperature recording and control meters and mercury vapor.

Of course, I think Mr. Hulsart deserves especial commendation for his remark about the doctor this morning. After a score of years of mercury experience, I have always been confronted with this bogeyman of danger. I am still looking for the fellow killed by mercury vapor. I have not found him yet. Maybe he exists somewhere; but I am sure I shall meet him in my after life.

The reliability of the mercury vapor system is now commensurate with that found in the steam boiler, so we do not need to worry about that. Expensive repairs are out.

Now, I want to emphasize one other thing: we glide over the work of years when we talk about the number of installations. Roughly, the aggregate rating of mercury vapor boilers in existence today and

operating daily, so far as I know in B. t. u.'s, both power and process, is one and a half billion B. t. u.'s per hour. Now we have to talk billions since our economic and political setup is such that we can't think of millions, and I just want to emphasize the fact that we have gotten into the billion B. t. u.'s per hour class, if not the billion dollar class.

Finally, when competitors meet, there is always a question about what part of the field shall go to each competitor. I do not think we can predict. I feel particularly that we go into too great generalities when we take any certain temperature range and say, "Above this the field belongs to this product; below this point to some other product." There probably are separate fields, but I doubt that those fields are separated by temperature alone. So many other things enter. Let us not, therefore, take any one group of products between certain temperatures as a general rule; let us take a particular application and see what other factors, other than temperature, enter. As Mr. McKeen tells us, mercury vapor operates at as low as 250 degrees F., which gets it almost into the steam competition class for certain applications. In other words, it is the detailed design of your equipment that throws the final ballot for or against the use of steam, organic compounds, or mercury.

F. F. CHAPMAN: Are you concerned at all about the supply of mercury available?

C. A. HULSART: No.

F. F. CHAPMAN: The production as I understand it is somewhat limited.

C. A. HULSART: No. That question comes up continuously. The supply can be made adequate to meet demands and in cases where large quantities have been required for power generation units there has been no appreciable increase in price.

D. R. KELLOGG: I can't produce the fellow killed by mercury, but I know of three cases where men were made extremely ill for a long period, one of them never fully recovered, and no one of whom at any time smelled mercury or felt acute discomfort therefrom. This was not in connection with the operation of a mercury boiler, it was in connection with the very low concentrations to which the men were subjected for some period of time. Now, two of those men have told me that they feel all right, one after a period of perhaps a year or so and the other after a period of two or three years and the third, to the best of my knowledge—I have lost track of him however—was still, after a period of perhaps five or six years, in very bad shape, and it is this chronic poison that has been the bogeyman that I have thought of more than anything else. Of course, it so happens that I have known of quite a few mild but chronic cases of poisoning, which are pretty hard to overcome. I do not think, in general, the mercury is going to come out and hit you with a sledge

hammer. I was just wondering what the chances are of its gradually causing trouble.

C. A. HULSART: If it is possible, I would just like to know what the conditions of the case were. Of course, if you are handling mercury in a confined room and continually doing it, you are apt to get some, but I do not know of any case where they would be handling mercury without proper ventilation.

I know, about three years ago, when I was assigned the job of following the commercialization of this mercury process, I made a tour of several places where they were using mercury continuously. I found when we first started our work there was one place using mercury where they were using overhead ducts and exhauster fans, and the man that was working there was working in this room and he was confined by himself, with his assistant, and nobody else was allowed in the room, and he had these fans and all sorts of containers to hold his mercury. About six years later, three years ago, when I went over the field to make an investigation of what they were doing today I went in this plant and asked to go to the room to see the man filling the different articles they were making with mercury, to see what they were doing now with regard to safeguarding the operator. The same operator was still there, but there were no fans and no ducts, and his remarks about those ducts were not fit to print. He did not want them, had them taken out, and he had been doing that work up to that time, I believe, for sixteen years, working in that room which was about fourteen feet by eighteen feet.

M. H. ITTNER: Mr. Chairman, Mr. Carlisle, who is sitting here, showed us at a former meeting how they could handle hydrocyanic acid on a large scale without any danger. I do not know why we are worrying so much about mercury.

CHAIRMAN MARSHALL: Any further questions? It just occurred to me, on the basis of Mr. Crosby Field's remark about meeting the man who died, there will have to be added to the staff of some of the operators of mercury plants a new type of technician, a mortician who is familiar with the Egyptian technique, so it will be available to Mr. Field.

We now come to the third paper of our morning session—"The Stroboscope and High-Speed Motion Picture Camera as Research Instruments," by Professor Harold E. Edgerton and Kenneth J. Germeshausen. The paper will be presented by Professor Edgerton.

THE STROBOSCOPE AND HIGH-SPEED MOTION-PICTURE CAMERA AS RESEARCH INSTRUMENTS

By HAROLD E. EDGERTON * and KENNETH J. GERMESHAUSEN †

I. Introduction

Time is an important element in engineering processes and projects as well as in the normal routine happenings of the day. Production processes, new developments, and experiments of all kinds are scheduled, judged, and recorded as functions of time in units of years, months, weeks, days, hours, minutes, or seconds. For instance, the construction of a large building may require a year, and during this time charts showing the daily progress of the work are carefully recorded and studied by the constructors to guide them in finishing the work within the scheduled time interval. As another example, the motions of the hands of a girl assembling the elements of a radio tube are carefully studied in order to reduce lost motion and the time required for the construction of the tube. Since the hands move so quickly that some of the actions are lost to the eye of the observer, it has been common practice to use slow-motion pictures for the purpose of motion study. Such pictures taken, say, at 64 frames per second and projected at 16 per second, show the action slowed down by a factor of four, and make it possible to see motions normally lost to the eye. Furthermore, a study of the individual pictures themselves, frame by frame, often brings out obscure but important details. Similar motion studies of fast machinery are difficult because equipment is not commonly available for recording the information in a similar fashion.

The stroboscope and the stroboscopic-light, high-speed motion-picture camera are instruments of use especially in studying rapidly-moving objects, and the purpose of this paper is to discuss the ability and limitations of each in their application to engineering problems. The mercury-arc stroboscope lamps used in the particular type of stroboscopic apparatus described, were developed at the Massachusetts

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Institute of Technology in the Electrical Engineering Department, and successfully applied to the measurement of the oscillations of synchronous machines during transient conditions. Since then they have been applied to many other problems, a few of which will be described in this paper.

II. The Stroboscope

The stroboscope is applicable to the study of problems wherein the motions are periodic and of high enough frequency to utilize the

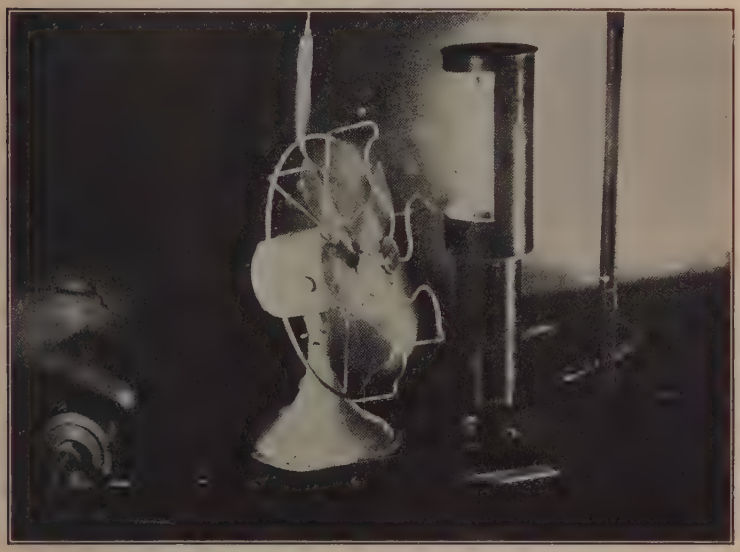

FIG. 1. A photograph showing a mercury-arc stroboscope illuminating an electric fan. The blades of the fan are visible in the photograph, although the continuous light shows a blur between the blades. A small piece of cloth saturated with titanium tetrachloride is used to produce smoke in order to investigate the flow of air through the fan blades.

persistence of vision. Since it is easy to use, it should be employed wherever possible in preference to photographic methods.

Stroboscopic effects have been understood for at least a century, but the usual optical methods of producing the intermittent light were not of a sufficiently practical nature to cause the device to be much more than a scientific toy. The first experiments involved the mechan-

ical interruption of a beam of light, either before striking a rotating object, or after being reflected towards the eye. A disc with a radial slit was often used as a shutter for the type just mentioned, and such a shutter has a low efficiency, especially if the slit is small, as it must be to obtain short flashes of light.

Flashes of stroboscopic light produced by electrical discharges in sparks, glow tubes, or arcs have several properties of great importance, particularly the great brilliance and the very brief duration of the flash. One type of circuit involves a spark coil with a neon tube connected to the high-voltage winding. As in automobile ignition work, the interruption of the current in the primary induces a high voltage across the secondary, which causes the neon lamp to glow for an interval of time whose duration depends in general upon the circuit constants. The disadvantages of this arrangement are that the electrical contacts need to open a large current, and that there is considerable loss of energy in the windings of the spark coil. A second type of circuit, of which the one [1,2] used by the authors is an example, makes use of a condenser discharge. Electrical charge is accumulated in a condenser in a manner analogous to its accumulation in a thunder cloud. The very sudden release of the charge results in a flash of lightning in the case of the cloud, and a flash of light in the mercury-arc stroboscopic lamp in the case of the condenser. The interval of time between the flashes of light from the stroboscope is usually controlled by a variable-speed rotating contactor, although any electrical pulse can be made to operate it either directly or after amplification. A flash of light from a mercury-arc stroboscope lamp lasts from 10^{-6} to 10^{-5} seconds, depending upon the capacity of the condenser, the voltage to which the condenser is charged, the temperature and dimensions of the lamp, and other factors. A description of a stroboscopic lighting source will be given in connection with the discussion of the motion picture camera.

The stroboscope depends upon the persistence of vision of the eye. The periodic flashes of light produced by the stroboscope are arranged to be at a frequency of approximately that of the object under observation. Consider, for example, a wheel rotating at a speed of 3600 revolutions per minute. Should the stroboscope be adjusted to 3600 flashes a minute, the wheel would appear absolutely stationary. With a flashing frequency of 3590 per minute the wheel would appear to rotate forward at a speed which is the difference of the actual speed

and the flashing speed, which in this case is 10 per minute—a speed which may be easily counted. Likewise, should the flashing speed of the light be greater than the rotation speed, then the wheel will appear to rotate backwards at a speed which again is the difference. Small

Fig. 2. Three enlarged frames from a 35-mm. motion picture showing a close-up view of the smoke (see Fig. 1) as it forms vortices on the ends of the blades. Taken with a standard 35-mm. camera, f3.5 lens, supersensitive panchromatic film.

irregularities in the speed of the wheel are very evident, since they are directly observable instead of being superimposed upon the actual speed of rotation.

Other motions than those of rotation are observable with the strob-

oscope. In this classification are springs, wires, braces, beams, liquids, the flow of air through fan blades and compressors, the vibration of crank shafts, and innumerable other moving parts. The requirements are that the motion shall be both (1) periodic, and (2) of sufficiently high frequency to use the persistence of vision. Speeds below about 960 per minute are difficult to observe with a stroboscope, because the eye fails to hold over the images and is bothered by the flicker. A bright stroboscopic light source in a very dark room makes it possible to see even down to as low as 100 revolutions per minute, although the result may be far from satisfactory. The high-speed motion pictures are useful for cases involving these low speeds, and will be taken up later.

A great many times in engineering work it becomes important to read the speed of an inaccessible part or a light delicate member which would be very appreciably slowed down by a tachometer. The stroboscope is an ideal instrument for reading speed in either of these cases and many others, the only requirement being that the object can be seen. All that is necessary is to adjust the frequency of the stroboscopic light until the object appears stationary, since when this is true, the speeds of the two are identical. A determination of the speed of the commutator immediately results in a determination of the speed of the object. One word of caution is necessary. The speed of the object may be a multiple of the speed of the commutator, since the object may rotate two times, three times, etc., between flashes and yet appear the same to the eye. It is impossible to get a fundamental stationary pattern with flashing speeds greater than the actual speed. Therefore, if the speed of the stroboscope is continuously raised, the highest speed which will give a stationary fundamental pattern is that which corresponds to the speed of the object. Usually the approximate speed is known; for instance, a spindle in a textile plant goes approximately 10,000 revolutions per minute.

A symmetrical radial pattern such as is given by a wheel with a number of evenly spaced spokes, may sometimes give erroneous results, since the spokes may be sufficiently identical to be confusing to the eye because of their similarity. Confusion of this sort is easily avoided by painting or marking with chalk one of the spokes or making a mark on the rim. Oftentimes these symmetrical patterns give useful relationships, since the number of identical elements around the circle, k, the speed of rotation, R, and the frequency of flash, F, are related

by a simple equation for the case giving an apparently stationary pattern.

$$Rk = Fn$$

where R = speed in r.p.m.
F = flashes per minute.
k = number of elements.
n = any integer such as 1, 2, 3, 4, etc.

A more detailed explanation of this equation and its application is given in one of the references.[2]

A few of the outstanding examples of uses of stroboscopic light are listed below:

(1) *The study of vibrations.* By means of the stroboscope it is possible to study in detail the nature of vibrations, to measure their frequency, to determine the time-phase relationship to the disturbing force, and to measure the amplitude.

(2) *Tachometer.* As has been described, one of the most obvious uses of the stroboscope is to measure speeds.

(3) *Meter calibration.* A standard watthour meter[3] is employed to time the interval between the flashes of light. The stroboscopic light shining upon the meter to be calibrated enables the tester to immediately adjust the setting until the dial appears to be stationary, at which time the two meters are running at identical speeds.

(4) *Watch adjustment.* A constant frequency may be used to trip a stroboscope lamp for quickly adjusting the regulation of a watch. The development of a scheme of this type[4] was recently announced.

(5) *Observation and adjustment of periodic production operations.* In this classification are envelope folders, bread slicers, packaging machinery, paper cutters—where registration of the cutter with a design is important—and multicolor printing on paper and cloth.

(6) *A high-speed clock hand.* The General Radio Company uses a stroboscopic lamp so arranged as to be flashed by the time signals from Arlington. A hand on the clock, rotating ten times per second, permits comparison of times to be made to an accuracy of 1/5000th of a second.

III. High-Speed Motion Pictures

There are many events in this life that happen too quickly to be seen by the unaided eye. Either too much information is presented in

too short a time for the brain to record, or the motion of a particular object is too rapid for the eye to follow.

It has been seen that the stroboscope is useful in slowing down repetitive or periodic events, but for those events that do not repeat at regular intervals with a frequency of greater than about 16 a second, the high speed camera is the only tool at present available to enable the eye to see what is happening.

Motion pictures of this type are taken with the camera driven at a rate greater than normal, and are then projected at the usual rate. The projected picture shows the motion of the subject slowed down by that ratio by which the camera was speeded up.

Further than allowing one to see the event at a reduced speed, high-speed photography enables one to make accurate measurements of velocities, accelerations, and displacements. If motion pictures of an event are taken and the time between successive pictures is accurately known, displacements between successive pictures can be measured, and, since the time is known, it is possible to compute the acceleration and velocity.

A short exposure time is important for measurements of the type described above, since a short exposure reduces the blur of the image of the moving object on the film. Stroboscopic photography with its exposures of less than one one-hundred-thousandth of a second is particularly useful in measurements of the motions of high-speed objects. For instance, the golf ball velocity study which is given later as an example would be very difficult if the exposures were even as long as one ten-thousandth of a second, since the ball would move about 1/4 of an inch (about 1/6 of the diameter of the ball) during the exposure time.

It seems to be impractical to speed up the ordinary intermittent motion-picture mechanism to speeds much greater than ten times normal because of inherent mechanical difficulties. Thus, in general, it may be said that all types of high-speed cameras for speeds greater than about 160 pictures per second must utilize continuously-moving film instead of intermittently-moving film. There are two types of continuously-moving-film cameras:

(1) Those employing a moving optical system to keep the image stationary with respect to the film during the exposure time.

(2) Those employing an intermittent source of stroboscopic light

whose flashes are of sufficiently brief duration to give a sharp image on the moving film.

Each of these two types of camera has its advantages and disadvantages which need to be carefully considered with respect to the particular problem at hand. The first type of camera[6,7,8] is especially adapted to the study of subjects which produce their own light, common examples of which are the burning of vapors, the action of

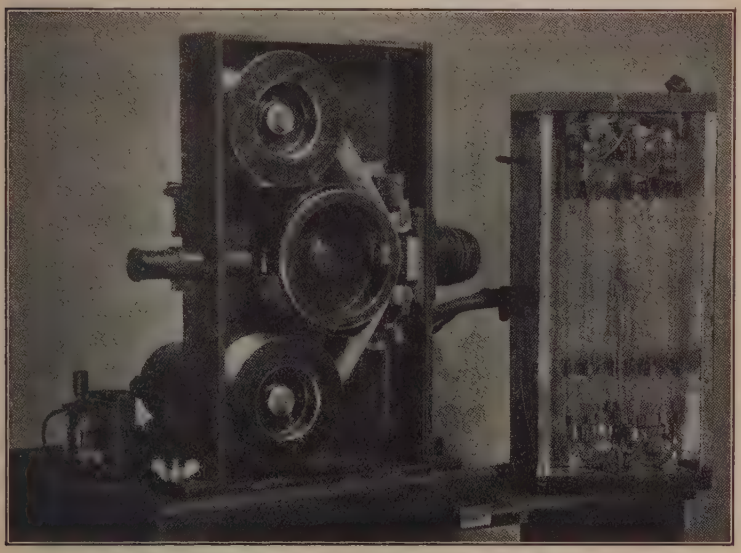

FIG. 3. A photograph of a continuously-moving-film, high-speed, motion-picture camera which takes 35-mm. pictures at speeds up to 1200 per second, and a bank of four mercury-arc lamps for providing the illumination.

explosives, the motions of an electric arc, the reactions in a photoflash bulb, and the behavior of the cathode spot in a mercury arc. The stroboscopic-light type of camera is of very limited use in the study of problems such as these.

The principal advantage of the stroboscopic-light type of camera over the moving-optical-system type is the short exposure time which effectively stops the motion of rapidly-moving objects during exposure. The stroboscopic light gives an exposure time of a few millionths of a second, which is considerably shorter than is feasible by the moving-optical-system method, especially since as long an exposure

as possible is usually desired in the moving-optical-system type in order to get sufficient density on the film. In high-speed cameras employing stroboscopic light the film is moved past the lens at a constant speed, and each time the film has moved the distance occupied by one picture, the subject is illuminated by a short brilliant pulse of light. The time at which the flash occurs is controlled by a commutator rigidly attached to the film-driving mechanism, and the duration of the flash is so short that no appreciable blurring of the picture occurs. The particular type of stroboscopic-light, high-speed motion-picture camera developed at the Massachusetts Institute of Technology will now be described.

IV. The Source of Stroboscopic Light and the Camera

Condenser discharges into mercury-arc lamps have proved to be a very useful manner of obtaining stroboscopic light for photographic work. The light is actinic, the discharge time is short, the timing is susceptible to accurate control by means of pulse amplifiers, the construction of the tubes is relatively simple, and as many tubes may be connected in parallel as desired, since they all flash at the same instant.

Fig. 3 shows one bank of mercury-arc stroboscope tubes with four lamps, and the high-speed camera.

The wiring diagram of the apparatus in Fig. 3 for taking high-speed motion pictures is shown in Fig. 4. A six-phase, 10-kw. rectifier unit supplies 1000 volts d-c. to charge the condensers. Resistors in series with each condenser limit the flow of current to the lamp in case of holdover, but still allow the condensers to become effectively charged during the interval between flashes.

The lower part of the circuit shows the diagram of the pulse amplifier, which makes it possible for a small impulse from the brush to snap on the large mercury-arc lamps. Connecting the two wires which go to the commutator trips the thyratron and it permits the discharge of the energy stored in the condenser C into the step-up transformer T. The external starting bands of several of the tubes may be connected in parallel, as shown, or separate transformers may be used for starting each tube or bank of tubes.

The camera shown in Fig 3 was purposely designed to eliminate any sliding motion of the film against a gate or other parts, since scratches, heat generation, and electrostatic voltages are caused by friction. The disadvantage of the type shown is that the pictures

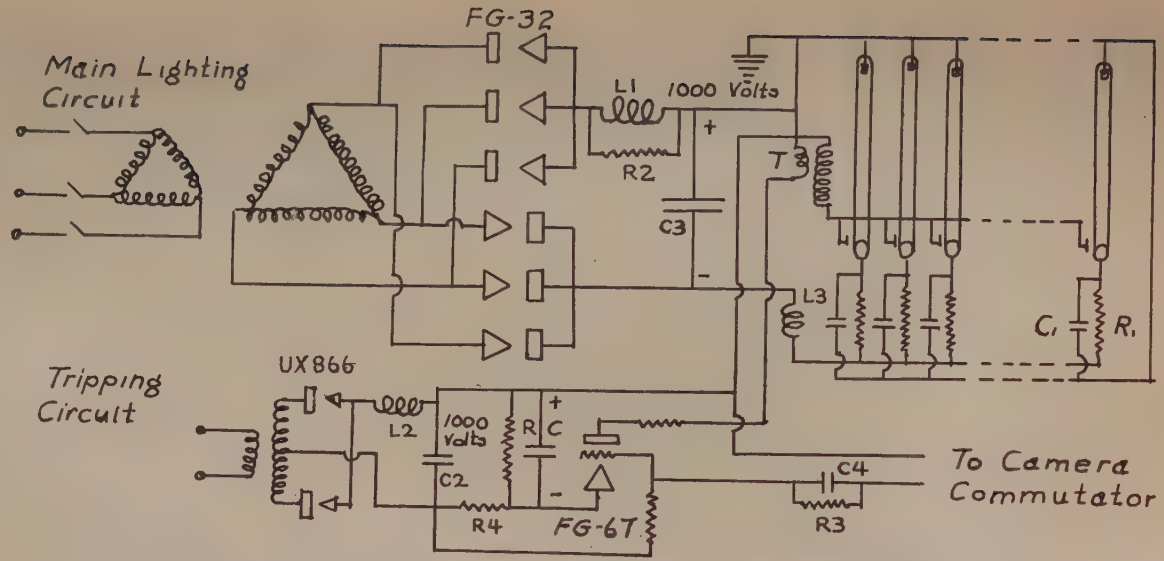

FIG. 4. Wiring diagram of a stroboscopic lighting source for taking high-speed motion pictures.

TYPICAL VALUES OF THE CIRCUIT CONSTANTS

C	0.125 mf	1000 volt	R	100,000 ohms	L_1	0.2 henry.
C_1	2. "	1000 "	R_1	400	L_2	5 henries.
C_2	10. "	1000 "	R_2	300	T	40:1 transformer.
C_3	50. "	1000 "	R_3	2 megohms	L_3	.003-.001 henry swinging choke.
C_4	.0001 "	5000 "	R_4	1500 ohms.		

are taken upon the film while it is on a curved surface. Whether or not there is any appreciable distortion depends upon the diameter of the sprocket and the size of the frame. A compromise is made also between a very large clumsy sprocket (and incidentally, a large camera with its difficulties of acceleration) and a small sprocket with its distortion. A consideration of these factors gave the main sprocket a diameter of approximately five inches with twenty standard 35-mm. frames of film around its periphery. For this sprocket the center of the picture is 0.0295 inch closer to the lens plane than the extreme upper and lower edges of the frame. This distance is naturally smaller for pictures shorter than the full 35-mm.-frame height. Two square holes exactly the size of a 35-mm. frame are diametrically placed in the sprocket for the purpose of alignment of the camera and for critical focusing of the lens, which is accomplished by the aid of a telescope located in the back of the camera. This method has been found to be very effective, since the focus and line-up may be easily and accurately checked just before the camera is started. Many subjects are very close to the camera, and for this reason a small displacement of the camera or subject will disturb the focus.

Considerable care is required in the construction of the commutator, since the uniformity of framing depends on the perfection of the commutator and brush rigging. As shown in the photograph of the camera, the commutator is on the same shaft as the sprocket and is located outside the box in order to be readily inspected. Brush construction is important, since any vibration or bouncing will cause a non-uniform spacing of the frames. This camera has small stranded copper brushes about 1/16 inch in diameter. They are pressed against the commutator by springs. Adjustment is possible so that the location of the frame with respect to the sprocket holes may be determined. Since there is an inappreciable time lag in the electrical circuit after the segment hits the brushes, the brush adjustment is made with the camera at rest.

The driving motors have been selected to give rapid acceleration and to hold fairly constant speed after the film has been accelerated. A series motor is directly connected to the take-up reel at the bottom of the camera. It is operated on overvoltage in order to increase its accelerating torque so that it always tends to overdrive the film. The series motor contributes considerable acceleration to the main sprocket and to the supply reel, besides performing its function of reeling up the film as it comes through the camera. A three-phase,

¼-H.P. induction motor is belted to the camera shaft with a V belt. A belt is used because of the ease of changing speed by using different pulleys. The motor is started with overvoltage in order to increase the acceleration torque. The speed-torque characteristics of the induction motor are such that the motor tends to run at a constant speed corresponding to the speed of the rotating field set up by the current in the armature windings. Since the load is small after the acceleration period, the motor will run fairly close to synchronous speed, and the rate of taking the pictures is thereby fairly constant and known. The film reaches a speed of 75 ft. per second in about 10 ft. of film.

V. Uses of the High-Speed Camera

The most obvious use of the high-speed camera is for taking motion pictures of fast or complicated motions in order that that motion may be slowed down, when projected on the screen, to such a speed that the eye is able to see and the mind to comprehend. Such motion pictures may of course be projected repeatedly, and often subsequent showings bring out details which were not noticed in preceding projections.

The best speed of taking the pictures depends upon several factors, but in many cases pictures taken at several speeds also prove useful. A slow picture shows the slow part of an action in detail, while a faster one shows more clearly the faster part of an action. Take, for instance, a picture showing the action of a sewing-machine needle. Relatively slow pictures are used to show the general motion of the needle, while pictures of much higher speed are needed to show details of the stitching, since it occurs during a short portion of the cycle. A rough but helpful calculation may usually be made when deciding upon a speed for taking the pictures, if the approximate speed of the motion is known, since the desired time for the final projected action should be from three to eight seconds.

Another equally important use of the high-speed motion-picture camera is for obtaining engineering data and measurements. The individual frames on the moving-picture film record as a function of time the instantaneous positions and the form of the object being photographed. In this respect the high-speed motion-picture camera is for a mechanical engineer an instrument analogous to the oscillograph for the electrical engineer, since the oscillograph furnishes curves of current, voltage, and power as functions of time.

FIG. 5. High-speed motion pictures taken at 960 per second, of the impact of a golf club and ball for the purpose of measuring the velocities involved.

The velocity of a moving object may be measured from a motion-picture film by measuring the difference in the position of the image between two successive pictures and dividing by the time interval between the pictures. The accuracy of the final result is influenced both by the accuracy of measurement of the displacement and the accuracy of determination of the time interval. Usually the former introduces the larger inaccuracy because of the difficulty of measuring the displacement due to the small size of the pictures, the blur if the exposure is long, and the size of the silver grains. The film shrinks as it becomes dry, and so the photographs should have a distance reference upon them in order that the result of the measurement may be independent of the state of the film. The accuracy of velocity determination is improved by taking close-up pictures giving larger displacements between images. The short exposure time of the stroboscopic light is especially advantageous for velocity measurements, since the pictures are not blurred by motion of the object during exposure.

Acceleration measurements follow from the velocity determinations, since the acceleration is the change of the velocity with time. The slope of the velocity-time curve is therefore the acceleration, and the accuracy of measurement is dependent upon the accuracy of the measurement of velocity and time, with the additional difficulty of measuring the slope of a curve.

A very good example to illustrate the method of measuring velocities is the analysis of a golf stroke. Fig. 5 is a series of instantaneous pictures taken at a rate of 960 per second. The velocities of the ball and club are obtained by measuring the displacement between pictures and then multiplying by 960. Measurements of displacements by means of a comparator permit the determination of the velocities of the club and ball, both before and after impact, with an accuracy of about 2 per cent. An analysis of the photograph shown as Fig. 5 resulted in the following data:

Initial club velocity just before impact ..	151 ft./sec.
Final club velocity just after impact	114 ft./sec.
Ball velocity	186 ft./sec.
Spin of the ball	5000 r.p.m.

Since the mass of the ball and the club are known, there is sufficient information to calculate the energy lost by the club-head and the

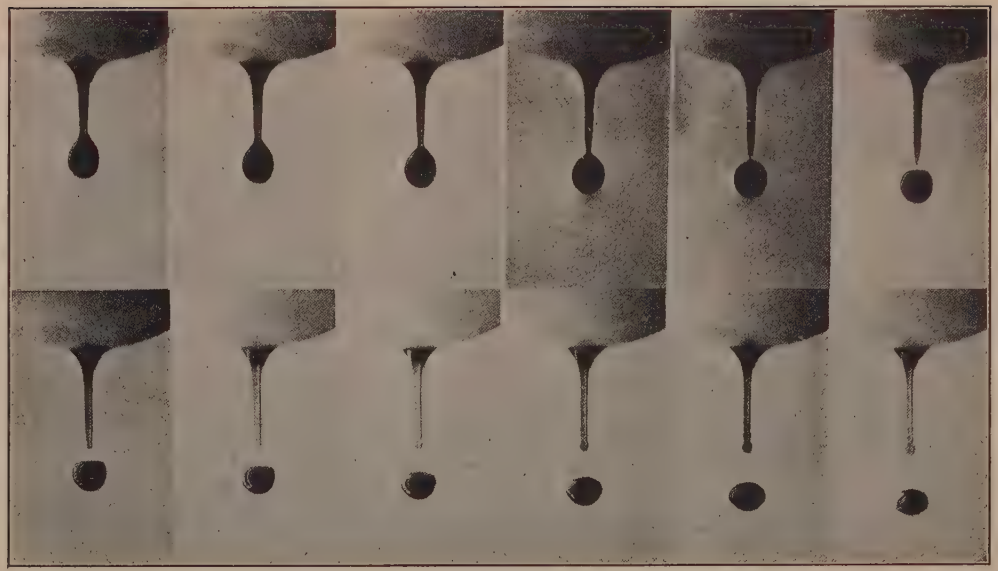

FIG. 6. A series of photographs taken from a high-speed motion picture (500 frames per second) showing the formation of a drop of water (slightly colored with ink) on the bottom of an electric-light bulb.

energy gained by the ball, as well as to calculate the energy stored in rotation. The pictures show definitely that the ball and club are in actual contact for less than 1/1000th of a second since the impact occurs during the interval between pictures. It is not possible to measure the accelerations of the club and ball from these pictures since the acceleration of the ball was completed between frames.

VI. The Application of High-Speed Photography to Chemical Engineering

The applications of the stroboscope and the high-speed camera are probably not as extensive in chemical as they are in certain other fields of engineering, but there are cases where these instruments should be useful. A few possibilities are enumerated below, which are the outcome of suggestions by chemical engineers, and other applications may occur to the reader. Many of these problems are mechanical in nature, but they are intimately tied up with chemical-engineering processes.

In chemical engineering there are some cases of very high-speed machines. The first type to consider are those depending on centrifugal force. High-speed photography should enable one to study the travel and behavior of crystals and other materials in the basket of a rapidly-rotating centrifuge. This study should help in solving problems of centrifuge design. Similarly, the breaking of emulsions by centrifugal means could be studied. Lines of flow, dead spaces, etc. in centrifugal pumps also could be studied in this way and should help in designing better pumps.

Vibration problems are another type where high-speed photography is valuable. These fall into two groups: first, where vibration is desirable and is to be utilized to the greatest possible extent; second, where vibration is undesirable and should be prevented as far as possible. In the first group there are many examples, such as motion and formation of fibers on a vibrating wire of a paper machine, motion of ground particles on a vibrating screen for sifting, motion of particles on a vibrating table for ore classification, behavior of liquids subjected to sonic or ultrasonic vibration, etc. In the second type the information obtained by photographs should help in eliminating undesirable vibrations.

Colloid mills are a type of very-high-speed equipment. Here

special mills would have to be built with transparent plates and housing. High-speed photographs of materials passing through such mills should give very valuable information concerning the action of such mills.

Vane pumps are slower-acting, but a study of such pumps, built with transparent sides, would give valuable data on how the vane follows the wall. Such data would be very useful in designing pumps.

One very common problem in chemical engineering which lends itself particularly to high-speed photography is that of getting intimate contact between a liquid and a gas. This problem arises in many places and in many forms, such as in sprays which are used to obtain intimate mixtures of fuels and air for combustion; for obtaining intimate mixtures of water with air for cooling, washing, or humidification; for obtaining intimate mixtures of a liquid and a gas which are to react. Foams, bubbles, and froths such as are used in fractionating towers to obtain intimate mixtures of ascending vapors and descending reflux liquid, in absorbers to obtain intimate contact between the gas and the washing liquid, etc., present similar problems. The formation, travel, and bursting of the gas bubbles and the travel of the liquid could be studied by means of high-speed photography. While considering the question of bubbles, foams, and froths, it is desirable to consider the study of their formation and utilization in the floatation of ores, in firefighting, and in beverages.

The problem of rupture is of great importance to chemical engineers, particularly brittle rupture. This again comes under two heads: first, where rupture is desired, as in crushing and grinding; second, where resistance to rupture is desired, as in the case of most manufactured materials. In the case of brittle materials rupture comes very suddenly with but little previous deformation. Exactly what happens at the instant of rupture can be determined only by high-speed photography. This photographic study would enable one to tell the amount of deformation taking place just before rupture; directions of rupture, cleavage planes, etc.; general behavior of body at rupture. This knowledge should enable one more intelligently to design mills and crushers to get the maximum rupture for the energy expended, to design brittle equipment (glass, ceramic materials, quartz, enamels) so as to get the maximum resistance to rupture, and to study various materials to see which would best withstand different types of strain or impact.

The problem of elastic and plastic deformation under impact of resilient materials is similar to that of rupture. The manufacture of such materials is constantly becoming more important, rubber and its compounds, synthetic resins, and other molded plastics, gutta percha, and others. A photographic study of these materials under impact would no doubt give a valuable check on their fitness for various purposes.

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Discussion

Chairman Marshall: The paper is now open for discussion. If there are no questions we will adjourn and proceed with our business session. (See Bulletin of Proceedings No. 48.)

FRACTIONAL DISTILLATION

I. Methods for Determining the Number of Equilibrium Plates

By GEO. GRANGER BROWN,* and MOTT SOUDERS, Jr.*

Fractional distillation is one of the most important unit operations of chemical engineering and as such has received considerable attention. But as yet no wholly satisfactory treatment has appeared for the design or test of such equipment operating on mixtures of more than two components. The method suggested herein has been found convenient and sufficiently reliable in some rather difficult cases that could be handled in a practical manner by no other available method, and is presented as a step toward a simple and satisfactory method for determining the number of places required when fractionating complex mixtures.

Fractional distillation may be defined as the process of separating a mixture of two or more components into fractions of narrower boiling range by means of successive vapor-liquid contacts and separations. Therefore consideration of the mechanism of vaporization and condensation will aid in understanding the process of fractional distillation.

Vaporization is the change from a more dense phase (usually liquid) to the less dense vapor phase in a system composed of two phases. If the vapor so formed in a partial vaporization of a multicomponent mixture is different in composition from the residual liquid, as is usually the case, the vapor becomes richer in more volatile components and poorer in less volatile components, and the residual liquid becomes richer in less volatile and poorer in more volatile components than the original liquid before vaporization. If the mixture is heated to a temperature at which it is completely vaporized under the prevailing pressure, the vapor will have the same composition as the original liquid.

Condensation is essentially the reverse of vaporization, the condensate being richer in less volatile and poorer in more volatile components and the remaining vapor being richer in more volatile and

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poorer in less volatile components than the original vapor, unless the vapor is all condensed. Under equilibrium conditions the ratio of mole fraction of a component in the vapor phase to that of the same component in the liquid phase is equal to the equilibrium constant

$$K = \frac{y}{x} \tag{1}$$

Under conditions where the ideal gas, and Raoult's Laws may be applied

$$K = \frac{y_a}{x_a} = \frac{p_a}{P} \tag{1a}$$

Under other conditions K must be known from equilibrium data or estimated by other means.[11, 33, 67, 71]

Fractional distillation consists in successive vaporization and condensation carried out continuously and simultaneously in a "column" such as the familiar bubble-plate column in which each plate acts simultaneously on the counter-current vapor and liquid streams as a partial condenser and as a partial vaporizer respectively. Ascending vapors come into intimate contact with cooler liquid so that less volatile components are partially condensed from the vapor and more volatile components are partially vaporized from the liquid. Thus the ascending vapor gains incrementally in more volatile components and the descending liquid in less volatile components.

The operation of such a column depends upon the difference in composition between the vapor and liquid and their relative quantities leaving each plate.

General Equations

The following equations obtained by material balances are familiar and given here for later reference.

$$F_L + F_V = F = D + B \tag{2}$$

$$a_F = a_D + a_B \tag{3}$$

$$x_F F_L + y_F F_V = x_D D + x_B B \tag{3a}$$

$$V_{n+1} = L_n + D \tag{4}$$

$$y_{n+1} V_{n+1} = x_n L_n + x_D D \tag{5}$$

$$\bar{V}_m = \bar{L}_{m-1} - B \tag{6}$$

$$y_m \bar{V}_m = x_{m-1} \bar{L}_{m-1} - x_B B \tag{7}$$

For practical purposes, the assumption* that L and V are constant throughout the rectifying section and $\bar{L}$ and $\bar{V}$ are constant throughout the stripping section is almost essential for convenient treatment of complex mixtures. For closely related substances such as the components in the feed to a natural gasoline stabilizer, the assumption may be substantially correct.

$$y_{n+1} = \left(\frac{L}{V}\right) x_n + \left(\frac{D}{V}\right) x_D \qquad (8) \text{ from } (5)$$

$$y_m = \left(\frac{\bar{L}}{\bar{V}}\right) x_{m-1} - \left(\frac{B}{\bar{V}}\right) x_B \qquad (9) \text{ from } (7)$$

$$\bar{L} = L + U \qquad (10)$$

$$\bar{V} = V + U - F \qquad (11)$$

When the feed is all liquid at the temperature of the feed plate, $F_L = F$ and $U = F$, so that $\bar{V} = V$ and $\bar{L} = L + F = V + B$.

When the feed is all vapor at the temperature of the feed plate, $F_V = F$ and $U = O$, so that $\bar{L} = L$ and $\bar{V} = L - B = V - F$.

An additional relationship is available from the fact that the sum of the mole fractions of the individual components in any mixture is equal to unity.

The Operating Equations

Equations (8) and (9) may be regarded as operating equations for the individual components. The slope (L/V) of each of the rectifying operating equations (8) is identical for all components, but the intercept $(D/V)x_D$ is different for each individual component. The slope $\left(\frac{\bar{L}}{\bar{V}}\right)$ of the stripping operating equations (9) is also constant for all components, and is related to the slope of the rectifying equation by the relationships (10) and (11), from which,

$$(F - U)y_a + Ux_a = a_F = y_{a_F} F_V + x_{a_F} F_L \qquad (12)$$

* This assumption is of much more general application than Trouton's rule which is usually given as the basis for the assumption and which merely states that the ratio of molal latent heat to absolute temperature is a constant for many different substances in the pure state. Even when Trouton's rule does not apply (as near the critical temperature of a component), the assumption of constant L/V may be valid.

in which y_a and x_a are common solutions for the rectifying and stripping operating equations and give the locus of the intersection of the two operating lines. When the feed is all liquid at the temperature of the feed plate the intersection lies on the vertical line, $x = x_F$. When the feed is all vapor at the temperature of the feed plate the intersection lies on the horizontal line, $y = y_F$. For a feed which is a mixture of liquid and vapor

$$y_a = -\frac{F_L}{F_V} x_a + y_{a_F} + \frac{F_L}{F_V} x_{a_F} \qquad (12a)$$

Equation (12a) is the equation of a line[12, 51] on the y, x plot having the slope, $-\frac{F_L}{F_V}$, and passing through the point x_{a_F}, y_{a_F}.

If the reflux returned to the column (x_o) has the same composition as the distillate (x_D), $y_1 = x_o = x_D$ and the rectifying operating line intersects the line $y = x$ at $x = x_D$. Similarly if the vapor returned to the column (y_{m+1}) has the same composition as the bottoms (x_B), or if the reboiler is assumed to be the bottom theoretical plate of the column, $y_{m+1} = x_m = x_B$, the stripping operating line intersects the line $y = x$ at $x = x_B$.

Minimum Reflux

In the special case of minimum reflux, i.e., infinite plates, the two operating lines intersect on a point of equilibrium as given by Equation (1) which is the equilibrium of the feed plate, or the intersection occurs on the equilibrium curve at the concentration on the feed plate. By solving Equation (12) for x_a and y_b (the point of intersection of the operating lines), the minimum values of the ratios L/V or L/D may be determined as the value necessary to make the sum of the mole fractions of the individual components in the liquid or vapor leaving the feed plate equal to unity.

METHODS OF CALCULATION

The methods which have been proposed for the calculation of the number of theoretical plates required may be classified into four general groups:

1. Algebraic calculation from plate to plate with provision for

variations in quantities of liquid and vapor flowing from plate to plate,

2. Algebraic calculations from plate to plate with the assumption of constant quantities of liquid and vapor,
3. Graphical methods which account for variations in the quantities of liquid and vapor,
4. Graphical methods which assume constant quantities of liquid and vapor.

Underwood [75] is recommended for an excellent critical review of various methods of calculation.

Binary Mixtures

Since a binary mixture represents the simplest problem in fractionation, most of the methods proposed for calculation of the number of theoretical plates have dealt with the separation of binary mixtures. Sorel [72] suggests an algebraic method which accounts for the variation in quantities of liquid and vapor flowing from plate to plate as do the graphical methods of Ponchon [58] and Savarit.[66] Algebraic methods which assume constant quantities of liquid and vapor include those of Ariis,[1] Bergstrom,[6] Gay,[27] Hausbrand,[28] Mariller,[49] Robinson,[62] Underwood,[75] and Van Nuys.[77] Graphical methods which assume constant quantities of liquid and vapor include those of Fouché,[26] McCabe and Thiele,[51] Rodebush,[63] Thormann,[74] and the nomographic method of Underwood.[75] The methods of Leslie [39] and Lewis [42] are essentially graphical integrations which assume small changes in composition from plate to plate, an assumption which is not justified unless the number of plates is large.

With those binary mixtures for which molal quantities of liquid and vapor are not constant, the advantageous simplification of the calculations arising from the assumption of constant quantities of liquid and vapor may be retained by expressing both compositions and quantities on the basis of equivalent quantities of heat instead of on the basis of molal relationships,[56] or in some cases where the molal quantities of liquid and vapor vary linearly with molal composition, average values of these quantities may be used.

The binary mixture is essentially a special simple case of the general problem of fractional distillation, because the temperature and the equilibrium compositions of the liquid and vapor phases are completely defined by the pressure and the concentration of one com-

ponent in either phase the phase-composition (y, x diagram) is independent of the vapor-liquid ratio or the number of equilibrium plates.

Complex Mixtures

Mixtures containing more than two components present two fundamental difficulties which are not present with binary mixtures. The concentration of a component in the vapor phase is not defined by the total pressure and concentration of the same component in the corresponding equilibrium liquid phase, as the entire composition of one phase is required in addition to define the temperature. The concentration of each component in the products cannot be chosen arbitrarily as with a binary mixture. All free variables are fixed when the pressure, reflux ratio (or number of plates), and two concentrations are chosen.[12] Any method dealing with complex mixtures is of value only in proportion to its success in surmounting these difficulties.

Thormann [74] and Young [79] have described graphical methods for three component mixtures in which the trilinear co-ordinates are used and the validity of Raoult's law [58] is assumed.

The methods proposed by Brown, Souders, and Nyland,[11, 12] Cope and Lewis,[18] Fenske,[24] Lewis and Matheson,[44] Thiele and Geddes,[73] and Underwood [75, 76] are among the principal general methods which have been proposed for calculating the number of theoretical plates required for the separation of mixtures containing more than two components.

Cope and Lewis [18] attempt to apply a graphical method similar to the method of McCabe and Thiele [51] to a complex mixture. On a plot the co-ordinates of which are y and x, Equations (8) and (9) represent the operating lines for the upper and lower sections of the column. The rectifying lines are parallel for all components as are the stripping lines. The vapor-liquid equilibrium is represented by Equation (1a). Since the pressure is, for all practical purposes, a constant, the equilibrium conditions of each component may be represented on the same plot as a series of straight lines passing through the origin with a slope equal to K. Each line represents equilibrium conditions for a particular temperature at the total pressure of the column. A different equilibrium line corresponding to a different temperature is used for each plate. Since the temperature is unknown, the proper equilibrium line must be found by trial and error so as to

make the sum of the mol fractions in each phase equal to unity. Starting with the overhead or bottoms composition, the composition from plate to plate is obtained by a stepwise construction between the operating and equilibrium lines.

Unfortunately, the concentration of only two components in either product may be assumed. The complete composition of the overhead and bottoms is a unique function of the operating conditions and the number of equilibrium plates and cannot be determined until the whole problem has been resolved. Although this method is simple in principle, it has all the inaccuracies of graphical manipulation, and is excessively laborious in practice if reasonably definite results are desired.

Lewis and Matheson [44] suggest an algebraic plate-to-plate calculation starting from overhead and bottoms compositions employing Equations (8), (9), and (1a). Equilibrium compositions at each plate are obtained by trial and error assumptions of plate temperatures until the sum of the mol fractions in each phase is equal to unity. The difficulty of obtaining consistent compositions of overhead and bottoms is minimized by assuming that only two components are distributed in appreciable quantities between overhead and bottoms; i.e. none of the more volatile components are present in the bottoms and none of the less volatile components are present in the distillate. This assumption is substantially correct when the separation between two adjacent components is relatively complete; i.e. the mol fraction of the more volatile distributed component in the bottoms, and the mol fraction of the less volatile distributed component in the distillate, are each relatively small quantities. In practice, however, this assumption introduces a further difficulty. Calculated compositions, for plates above the feed plate include none of the less volatile components, and for plates below the feed plate, none of the more volatile components.

To reconcile this inaccuracy, it is assumed that there is negligible change in composition between the feed plate and the plate above for more volatile non-distributed components, and between the feed plate and the plate below for less volatile non-distributed components. Under these conditions Equation (8) for the more volatile components becomes,

$$K_{a_f} \; x_{a_f} = \frac{L}{V} x_{a_f} + \frac{D}{V} x_{a_D}$$

$$x_{a_f} = \frac{\frac{D}{V} x_{a_D}}{K_{a_f} - \frac{L}{V}} \qquad (13)$$

and for the less volatile components Equation (9) becomes,

$$K_{d_f} \; x_{d_f} = \frac{\bar{L}}{\bar{V}} x_{d_f} - \frac{B}{\bar{V}} x_{d_B}$$

$$x_{d_f} = \frac{\frac{B}{\bar{V}} x_{d_B}}{\frac{\bar{L}}{\bar{V}} - K_{d_f}} \qquad (14)$$

By using Equations (13) and (14) to adjust the composition at the feed plate, the calculations may be carried out from the approximated feed plate composition working toward both top and bottom of the column. When difficulties are encountered as the top or bottom is approached, the composition of the feed plate is revised and by successive approximations of the compositions at the feed plate a satisfactory solution may eventually be reached.

The procedure is laborious and is limited to conditions where a relatively complete separation is to be made between adjacent components.

Fenske [24] attempts to eliminate the tedious plate-to-plate calculations by equations which give an overall solution based on terminal conditions. The method is designed to apply to two adjacent components between which the separation is relatively complete.

By dividing Equation (8) as applied to the more volatile distributed or cut component b by the same equation as applied to the less volatile cut-component c under conditions of minimum reflux when the difference is negligible between the compositions of liquids overflowing from successive plates near the feed plate, and by tacitly assuming a feed which is all liquid at the temperature of the feed plate, Fenske obtains the equation

$$\left(\frac{L}{D}\right)_{min} = \frac{1}{\frac{p_b}{p_c} - 1}\left[\frac{x_{b_D}}{x_{b_f}} - \frac{p_b}{p_c}\frac{x_{c_D}}{x_{c_f}}\right] \qquad (15)$$

Equation (15) is applicable only under conditions of minimum reflux (infinite plates) when the feed is all liquid and at the temperature of the feed plate.

Under conditions of total reflux, $y_{n+1} = x_n$, and F, D and B are each zero; and by equating the series of ratios obtained from Equations (8) or (9) applied to components b and c

$$\frac{x_{b_1}}{x_{c_1}} = \frac{x_{b_f}}{x_{c_f}}\left(\frac{K_b}{K_c}\right)^n \qquad (16)$$

$$\frac{x_{b_f}}{x_{c_f}} = \frac{x_{b_B}}{x_{c_B}}\left(\frac{K_b}{K_c}\right)^m \qquad (16a)$$

Where m equals the number of plates below feed plate, including the reboiler at the bottom, or kettle, as one theoretical plate. By assuming that the ratio of b and c in the liquid leaving the top plate is identical with the ratio of b and c in the distillate, and that the ratio of b and c in the liquid on the feed plate is identical with the ratio of b and c in the feed, Fenske calculates the minimum number of plates required under total reflux conditions.

These doubtful assumptions may be avoided by assuming that the reflux to the top plate has the same composition as the overhead vapor and that the kettle is the bottom plate of the column. Then the two Equations (16) and (16a) may be combined giving the overall equation,[75]

$$\frac{x_{b_D}}{x_{c_D}} = \frac{x_{b_B}}{x_{c_B}}\left(\frac{K_b}{K_c}\right)^{n+m+1} \qquad (17)$$

The equilibrium constants, K_b and K_c, may be taken as the mean values over the temperature range of the column. The exponent, $n + m + 1$, is the total number of plates, including the kettle as one theoretical plate, required for total reflux.

For calculating the number of plates required with intermediate reflux ratios, Fenske proposed other equations which he solves by making an assumption which is valid only for total reflux.

Fenske also states that a complex mixture is equivalent to a

binary mixture containing the cut-components in the same proportion as in the complex mixture. This simplification is valid only for total or minimum reflux. In general the complex mixture is equivalent to a binary mixture with a varying reflux ratio equal to

$$\frac{L}{D}\,\frac{x_{b_n} + x_{c_n}}{x_{b_D} + x_{c_D}}$$

a reflux ratio which varies from plate to plate and is a function of the other components present.[75]

Thiele and Geddes [73] propose an algebraic plate-to-plate calculation using the general heat and material balance equations such as (3) and (5). The number of theoretical plates is fixed at the start of the computations and curve of temperature distribution is assumed and modified by successive approximations. This method is more general than any of the methods previously described since it is predicated on fewer assumptions. But although valuable as a research method in analyzing operating data, it is too tedious to serve as a practical method of design.

Underwood's excellent paper [75] includes a stepwise method derived from ratios obtained by dividing Equation (8) for one component by Equation (8) for another component in conjunction with Equation (1) for the rectifying section.

$$\frac{\frac{L}{D}x_{a_n} + x_{a_D}}{\frac{L}{D}x_{b_n} + x_{b_D}} = \frac{K_a}{K_b}\,\frac{x_{a_{n+1}}}{x_{b_{n+1}}} = \frac{y_{a_{n+1}}}{y_{b_{n+1}}}$$

$$\frac{\frac{L}{D}x_{a_n} + x_{a_D}}{\frac{L}{D}x_{c_n} + x_{c_D}} = \frac{K_a}{K_c}\,\frac{x_{a_{n+1}}}{x_{c_{n+1}}}\text{, etc.}$$

Since for every plate $x_a + x_b + x_c \ldots\ldots\ldots\ldots = 1$

$$x_{a_{n+1}} = \frac{\frac{L}{D}x_{a_n} + x_{a_D}}{\frac{L}{D}N + C}$$

$$x_{b_{n+1}} = \frac{\frac{K_a}{K_b}\left(\frac{L}{D}\, x_{b_n} + x_{b_D}\right)}{\frac{L}{D} N + C}, \text{ etc.}$$

where $N = x_{a_n} + \frac{K_a}{K_b} x_{b_n} + \frac{K_a}{K_c} x_{c_n} + \frac{K_a}{K_d} x_{d_n} + \text{etc.}$

$$C = x_{a_D} + \frac{K_a}{K_b} x_{b_D} + \frac{K_a}{K_c} x_{c_D} + \frac{K_a}{K_d} x_{d_D} + \text{etc.}$$

Similarly for the stripping section by Equation (9),

$$x_{a_{m+1}} = \frac{\frac{K_a}{K_z}\left(1 - \frac{B}{\bar{L}}\right) x_{a_m}}{\bar{N}} + \frac{B}{\bar{L}} x_a$$

$$x_{b_{m+1}} = \frac{\frac{K_b}{K_z}\left(1 - \frac{B}{\bar{L}}\right) x_{b_m}}{\bar{N}} + \frac{B}{\bar{L}} x_{b_B}, \text{ etc.}$$

where $\bar{N} = \frac{K_a}{K_z} x_{a_m} + \frac{K_b}{K_z} x_{b_m} + \frac{K_c}{K_z} x_{c_m} + \ldots\ldots\ldots + x_{z_m}$

From the relationships so obtained the compositions on successive plates may be obtained starting with the liquid on the top plate in equilibrium with the overhead vapor, and with the bottoms, and working toward the feed plate.

By so working down from the top and up from the bottom the feed plate is found as the plate which satisfies the conditions

$$\frac{\frac{L}{D} x_{b_f} + x_{b_D}}{\frac{L}{D} x_{c_f} + x_{c_D}} < \frac{\frac{L}{D} x_{b_F} + \frac{U}{F} x_{b_D}}{\frac{L}{D} x_{c_F} + \frac{U}{F} x_{c_D}} <$$

$$\frac{\frac{L}{D} x_{b_{f-1}} + x_{c_D}}{\frac{L}{D} x_{c_{f-1}} + x_{b_D}} = \frac{K_{b_f} x_{b_f}}{K_{c_f} x_{c_f}} = \frac{y_{b_f}}{y_{c_f}} \qquad (18)$$

$$\frac{x_{b_f}}{x_{c_f}} > \frac{K_{c_f}}{K_{b_f}} \frac{\frac{L}{D} x_{b_F} + \frac{U}{F} x_{b_D}}{\frac{L}{D} x_{c_F} + \frac{U}{F} x_{c_D}} \qquad (18a)$$

in which b and c are adjacent components between which the separation is relatively complete.

The more volatile components which do not appear in the bottoms and the less volatile components which do not appear in the overhead are handled by adjusting the composition of the feed plate as calculated from the top to include the mol fractions of less volatile components as calculated from the bottom.

The minimum number of plates for total reflux is calculated from an equation similar to Equation (17).

Underwood's method is probably the least tedious and the most straightforward stepwise method of calculation which has been proposed. Even so, it is too laborious to be wholly satisfactory as a method of design, and it is limited in application to conditions where a relatively complete separation between adjacent components is to be made.

A simplified method suggested later by Underwood [76] is applied to two adjacent components between which the separation is relatively complete.

In this method, it is assumed that the ratio of the temperature drop in the rectifying section to the temperature drop in the stripping section is equal to the ratio of the plates in the two sections of the column, and that this ratio as calculated for total reflux may be used for any finite reflux ratio. The temperature of the feed plate is thus obtained from the top and bottom temperatures and Equations (16) and (16a). The composition of the liquid overflowing from the feed plate is then calculated by applying Equations (13) and (14) to all components except the cut components, by using relationship 18 with the cut components, and assuming that their mol fractions at the feed plate lie midway between their extreme limits.

This method is simpler than Underwood's original method because it starts from the feed plate, but is open to the objections that the ratio of number of plates in the two sections of the column may not be independent of reflux ratio and that the mol fractions of the cut components at the feed plate do not necessarily lie midway between their calculated limits. It may be applied only to conditions involving

a relatively complete separation between two adjacent components and hence is of limited availability.

ABSORPTION FACTOR METHOD

The absorption factor concept proposed by Kremser [38] and applied by Souders and Brown [69] to gas absorbers and oil strippers has been previously suggested [11, 12] as an apparent satisfactory basis for calculating fractionating columns.

The absorption factor method uses an absorption or stripping factor in an equation which involves the number of theoretical plates required over a section of a column to effect the change in terminal concentrations of an individual component. The method may be applied to one component at a time and is not limited to relatively complete separations between adjacent components.

If the quantities of ascending vapor and descending liquid are assumed to be constant, a material balance for any one component and around any plate above the feed, gives the equation,

$$y_{n+1} = y_n + \frac{L}{V} x_n - \frac{L}{V} x_{n-1}$$

Substituting the equilibrium Equation (1) ($y = Kx$) and the absorption factor, $A_n = \left(\frac{L}{K_n V}\right)$ the equation becomes

$$y_{n+1} = (1 + A_n)\, y_n - A_{n-1}\, y_{n-1}$$

Application of this equation to a number of successive plates leads to the general equation

$$y_{n+1} = (A_1 \cdot\cdot A_n + A_2 \cdot\cdot A_n + \cdot\cdot + A_n + 1)y_1 - A_1\,(A_2 \cdot\cdot A_n + A_3 \cdot\cdot A_n + \cdot\cdot + A_n + 1)K_1 x_0 \qquad (19)$$

If the absorption factor, A, is a constant the equation may be written

$$\frac{y_{n+1} - y_1}{y_{n+1} - K_1 x_0} = \frac{A^{n+1} - A}{A^{n+1} - 1} \qquad (20)$$

where y_{n+1} = concentration of any component in the vapor entering a section of the rectifying column;

y_1 = concentration of the same component in vapor rising from the top plate of the section;

x_0 = concentration of same component in liquid entering the top plate of the section;

K_1 = equilibrium constant for same component at the temperature of the top plate of the section;

n = number of theoretical plates in the section;

$A = \frac{L}{K_A V}$, for which K_A is the equivalent constant value of the equilibrium constant for the same component.

A similar derivation for a section of the stripping column leads to the equation

$$x_e = (1 + S_1 + S_1 S_2 + \cdots + S_1 \cdots S_m)\ x_m - S_m(1 + S_1 + S_1 S_2 + \cdots + S_1 \cdots S_{m-1}) \frac{y_{m+1}}{K_m} \qquad (21)$$

If the stripping factor, S, is constant, the equation becomes

$$\frac{x_e - x_m}{x_e - \frac{y_{m+1}}{K_m}} = \frac{S^{m+1} - S}{S^{m+1} - 1} \qquad (22)$$

where x_e = concentration of any component in the liquid entering a section of the stripping column;

x_m = concentration of same component in liquid overflowing from the bottom plate of the section;

y_{m+1} = concentration of same component in vapor entering the bottom plate of the section;

K_m = equilibrium constant for same component at the temperature of the bottom plate of the section;

m = number of theoretical plates in the section;

$S = \frac{K_S \bar{V}}{\bar{L}}$, for which K_S is the equivalent constant value of the equilibrium constant for the same component.

In setting up the conditions for a design problem for a given complex feed, only total pressure, reflux ratio, quantity of distillate, mole fraction of one component in the distillate, and mole fraction of another component in the bottoms may be fixed. All other compositions and quantities are dependent.[12] Usually, however, the more volatile components may be assumed to be absent from the bottoms and the less volatile components absent from the distillate, leaving only two or three components to be distributed between distillate and bottoms. Thus the compositions of the distillate and bottoms may be established without difficulty.

Temperature and Composition at Top Plate.—By neglecting, as conservative practice, any fractionation in the overhead condenser, the vapor rising from the top plate may be assumed to have the same composition as the overhead distillate. The equilibrium temperature at the top plate may then be calculated from the composition of the vapor.[33]

In many cases the temperature gradient between the plates at the top of the column is not linear. In such cases reliable results may not be obtained if the top plate is used as the upper terminus of the rectifying column, and it is advisable to compute by step-wise equilibrium calculations the compositions and equilibrium temperatures for one or two plates below the top or until the temperature gradient between successive plates is substantially uniform to determine a plate that may be used as a terminal plate for application of the absorption factor.

Temperature and Composition at Bottom Plate.—The composition of the liquid leaving the bottom plate may be calculated by assuming that the bottoms product is in equilibrium with the vapor entering the bottom plate and by making a material balance around the reboiler or kettle. The temperature difference between successive plates near the bottom is usually far from uniform, and it is advisable to continue the step-wise calculations up the column for a few plates until the temperature gradient approaches a linear relationship, to determine the bottom terminal plate for the stripping factor.

Temperature of Feed Plate.—Since the vapor rising from the feed plate is the feed to the rectifying section, and the liquid overflow from the feed plate is the feed to the stripping section, it is necessary to calculate the compositions at the feed plate depending upon the temperature of the feed plate. If it is assumed that the temperature

gradient between top and bottom terminal plates is linear, the temperature of the feed plate may be calculated from the equation

$$t_f = t_t + \frac{n}{n+m}(t_{bot} - t_t) \qquad (23)$$

where t_t = temperature °F. of top terminal plate

t_{bot} = temperature °F. of bottom terminal plate.

Since the number of plates above and below the feed is not yet known, this equation involves a trial and error procedure, which rapidly yields a satisfactory solution. When a relatively complete separation is to be made between two adjacent components, Equations (16) and (16a) for total reflux may be used to obtain a first approximation of the ratio $n/(n+m)$.

Composition at Feed Plate.—The computed composition of the liquid leaving the feed plate is made to fit the temperature of the feed plate estimated in the manner described. In order to fix this composition at the feed plate it is necessary to know the temperature and pressure and the concentrations of all but two of the components.

For components which do not appear in the bottoms it may be assumed that the mole fraction in the liquid leaving the feed plate is the same as that of the plate above so that Equation (13) may be applied. Similarly for components which do not appear in the distillate Equation (14) may be used.

When there are more than two components which appear in both overhead and bottoms, Equation (13) may be applied to the most volatile component appearing in the bottoms if the mole fraction of this component therein is small and the ratio of the number of plates above the feed to the number below the feed (n/m) is greater than two. The smaller the mole fraction in the bottoms and the larger the ratio of plates, the more applicable is Equation (13).

Equation (14) may be applied to the least volatile component appearing in both overhead and bottoms if the mole fraction of this component in the distillate is small and the ratio n/m is less than one-third. The smaller the mole fraction in the distillate and the smaller the ratio of plates, the more applicable is Equation (14).

The mole fractions of all but two components in the liquid leaving the feed plate may be determined as described. The mole fractions of these two intermediate components may be determined from

the estimated temperature of the feed plate and the two relationships: (1) sum of mole fractions of all components in the liquid leaving the feed plate is unity; and (2) sum of the products of Kx for all components is unity. The equilibrium constants, K, are determined from the temperature and pressure of the feed plate and the two simultaneous equations may be solved for the mole fractions of the two components whose concentrations in the liquid leaving the feed plate are as yet undetermined.

Application of Absorption and Stripping Factors.—It is assumed that the rectifying part of the column acts as an absorber of the least volatile distributed component and that the stripping part of the column operates as a stripper of the most volatile distributed component.

The value of the average or equivalent equilibrium constant K_A, of the absorption factor, A, for the least volatile distributed component may be taken as the average value between the upper terminal plate and the plate immediately above the feed plate.

$$K_A = \frac{K_t + K_{f-1}}{2} \qquad (24)$$

The temperature of the plate above the feed plate

$$t_{f-1} = t_f - \frac{1}{n+m}(t_{bot} - t_t)$$

The value of the equivalent equilibrium constant, K_S, for the stripping factor, S, for the most volatile distributed component may be taken as the average value between the plate immediately below the feed plate and the lower terminal plate.

$$K_S = \frac{K_{f+1} + K_{bot}}{2}$$

The temperature of the plate below the feed plate

$$t_{f+1} = t_f + \frac{1}{n+m}(t_{bot} - t_t)$$

Checking Assumed Temperature of Feed Plate.—When the number of equilibrium plates between the terminal plates above the feed plate, n, and below the feed plate, m, have been determined by means

of the absorption and stripping factor methods in the manner described, the assumed temperature of the feed plate is checked by using these values of n and m in Equation (23). If the temperature of the feed plate as originally assumed and the temperature determined from the calculated values of n and m differ by more than 3°F. it is usually necessary to make a new estimate of the temperature and repeat the calculation until the assumed and calculated temperatures agree within 3°F.

Discussion

The use of the absorption factor for the design or the calculation of fractionating columns according to the method outlined involves assumptions which can be justified only if they yield reliable results. The estimated composition on the feed plate is not precise, particularly when more than two components are common to, and present in appreciable concentration in both overhead and bottoms, but is much nearer the actual conditions than the simpler but misleading assumption that the composition of the feed itself might be used for the composition of the feed plate.[11,12] Although use of the feed composition gave satisfactory results in special cases, it is an unsound assumption and should not be used.

If the composition of the components to which the absorption factor is to be applied goes through a pronounced maximum between the terminal plates, the assumption of an average effective value for the equilibrium constant "K" as an arithmetric average between the terminal plates may lead to large errors, it appears that this difficulty may be eliminated by separating that part of the column into two sections with a terminal plate located at the maximum concentration of the components, or by applying the absorption factor method to a component which does not go through a maximum concentration between the terminal plates.

When reliable data are available from an operating column, it is not necessary to estimate the composition on the feed plate, and the column may be treated in a number of short sections, so as to avoid the necessity of making these two assumptions. When applied in this manner the absorption factor method as outlined should give reliable results in all cases.

When making a sharp separation between two adjacent components, the estimated composition of the feed plate and the method

as outlined are usually reliable provided the equilibrium data can be expressed in terms of equilibrium constants as is the case with ideal solutions. The convenience of the method is one of its most encouraging features, and it is hoped that the method can be developed so that it may be used with entire confidence for the design of fractionating columns as well as a means for analyzing operating data.

FRACTIONAL DISTILLATION

II. Theoretical Comparison of Methods of Calculation

By GEO. GRANGER BROWN* and MOTT SOUDERS, Jr.*
and WM. W. HESLER*

Because of the difficulty of obtaining actual experimental data on equilibrium plates, particular problems were set up and computed by stepwise calculations as a basis for comparison in determining the reliability of the absorption factor method All reliable methods of calculation must give substantially identical results when applied to the same problem.

Three-component mixtures of propane, butane and pentane were used for simplicity and because of available equilibrium data.[71] The pressure, and composition of the feed were fixed, the quantity of distillate, reflux ratio, and two mol fractions in products were chosen, and attempts were made to calculate the number of plates, the composition on each plate, and location of feed plate by stepwise calculation similar to the method suggested by Lewis and Matheson.[44] Many practical difficulties were encountered and had to be solved by trial and error before satisfactory results could be obtained in even a limited number of cases.

The quantity of distillate per unit of feed D/F must be chosen within limits which are frequently rather narrow if a material balance is to be obtained, with the same number of plates for each component.

Tables I, II, III, and Figures 1, 2, 3, give three attempts out of many to set up complete calculations when fixing the mole fraction of the least volatile component in the distillate at 0.01 and the mole fraction of the most volatile component in the bottoms at 0.01.

Tables IV, V, VI and Figures 4, 5, 6 give the results obtained when trying to design for 95.99% of propane, 4% of butane and 0.01% of pentane in the distillate (which is 30% of the feed) with a reflux ratio of 9. In this case it was found more convenient to start the calculations at the bottom. In each case a fairly satisfactory solution was obtained almost regardless of the feed plate location

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CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	.3333	.6566	.0100
Butane	.3333	.3333	.3333
Pentane	.3333	.0100	.6566
	.9999	.9999	.9999

Function	Value
D	0.5
B	0.5
L	4.5
V	5.0
$\overline{L}$	5.5
$\overline{V}$	5.0
L/V	0.9
$\overline{L}/\overline{V}$	1.1
D/V	0.1
B/$\overline{V}$	0.1

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

TABLE I

Plate No.	Plate Temp.	"K"@ Plate Temp.	Plate Composition, Mole Fraction, Vapor	Plate Composition, Mole Fraction, Liquid	Compound
1 Top	153°F.	1.46	.6566	.4500	Propane
		.65	.3333	.5130	Butane
		.28	.0100	.0360	Pentane
2	173°F.	1.69	.4707	.2835	Propane
		.81	.4950	.6270	Butane
		.36	.0334	.0960	Pentane
3	194°F.	1.85	.3208	.1735	Propane
		.95	.5976	.6290	Butane
		.445	.0874	.1965	Pentane
4 Feed	212°F.	2.02	.2218	.1096	Propane
		1.07	.5994	.5610	Butane
		.53	.1779	.3354	Pentane
5	235°F.	2.21	.1195	.0541	Propane
		1.23	.5837	.4740	Butane
		.65	.3032	.4670	Pentane
6	250°F.	2.35	.0585	.0249	Propane
		1.33	.4881	.3670	Butane
		.74	.4480	.6050	Pentane
7	265°F.	2.49	.0284	.0114	Propane
		1.43	.3704	.2590	Butane
		.83	.5998	.7240	Pentane

CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	.15	.47667	.01
Butane	.30	.51333	.20857
Pentane	.55	.01000	.78143
	1.00	1.00000	1.00000

Function	Value
D	0.3
B	0.7
L	2.7
V	3.0
$\overline{L}$	3.7
$\overline{V}$	3.0
L/V	0.9
$\overline{L}/\overline{V}$	1.233
D/V	0.1
$B/\overline{V}$	0.2333

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

TABLE II

Plate No.	Plate Temp.	"K"@ Plate Temp.	Plate Composition Mole Fraction Vapor	Plate Composition Mole Fraction Liquid	Compound
1	170°F.	1.62	.47667	.296	Propane
		.760	.51333	.675	Butane
		.334	.01000	.030	Pentane
2	185°F.	1.75	.3141	.1796	Propane
		.87	.6588	.7570	Butane
		.40	.0280	.0700	Pentane
3	196°F.	1.88	.2093	.1107	Propane
		.97	.7326	.7550	Butane
		.46	.0640	.1390	Pentane
4	212°F.	2.01	.1473	.0733	Propane
		1.07	.7310	.6830	Butane
		.52	.1260	.2423	Pentane
5	224°F.	2.12	.1136	.0536	Propane
		1.14	.6660	.5840	Butane
		.60	.2191	.3650	Pentane
6	238°F.	2.24	.0959	.0432	Propane
		1.25	.5769	.4640	Butane
		.675	.3295	.4900	Pentane
7 Feed	248°F.	2.33	.0865	.0371	Propane
		1.30	.4689	.3610	Butane
		.74	.4420	.5970	Pentane
8	260°F.	2.44	.0434	.018	Propane
		1.40	.3955	.283	Butane
		.80	.5540	.692	Pentane
9	270°F.	2.51	.0199	.008	Propane
		1.46	.2991	.205	Butane
		.86	.6711	.782	Pentane

CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	0.1500	0.47667	0.01000
Butane	0.3000	0.51333	0.20857
Pentane	0.5500	0.01000	0.78143
	1.0000	1.00000	1.00000

Function	Value
D	0.3
B	0.7
L	1.7
V	2.0
$\overline{L}$	2.7
$\overline{V}$	2.0
L/V	0.85
$\overline{L}/\overline{V}$	1.35
D/V	0.15
$B/\overline{V}$	0.35

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

TABLE III

Plate No.	Plate Temp.	"K" @ Plate Temp.	Plate Composition, Mole Fraction, Vapor	Plate Composition, Mole Fraction, Liquid	Compound
1 Top	170°F.	1.62	.4767	.2960	Propane
		.76	.5133	.6750	Butane
		.334	.0100	.0300	Pentane
2	185°F.	1.75	.3231	.1846	Propane
		.87	.6507	.7480	Butane
		.40	.0270	.0675	Pentane
3	194°F.	1.86	.2284	.1222	Propane
		.95	.7128	.7420	Butane
		.45	.0589	.1309	Pentane
4	205°F.	1.95	.1754	.0900	Propane
		1.04	.7077	.6800	Butane
		.495	.1128	.2280	Pentane
5	220°F.	2.09	.1490	.0720	Propane
		1.13	.6550	.5800	Butane
		.57	.1954	.3430	Pentane
6	230°F.	2.17	.1306	.0601	Propane
		1.20	.5700	.4750	Butane
		.625	.2931	.4690	Pentane
7 Feed	243°F.	2.28	.1226	.0537	Propane
		1.285	.4808	.3740	Butane
		.698	.4002	.5740	Pentane
8	255°F.	2.40	.0690	.0288	Propane
		1.365	.4319	.3160	Butane
		.77	.5014	.6520	Pentane
9	265°F.	2.48	.0354	.0143	Propane
		1.43	.3536	.2470	Butane
		.83	.6067	.7320	Pentane
10	271°F.	2.52	.0158	.0060	Propane
		1.45	.2605	.1790	Butane
		.87	.7147	.8200	Pentane

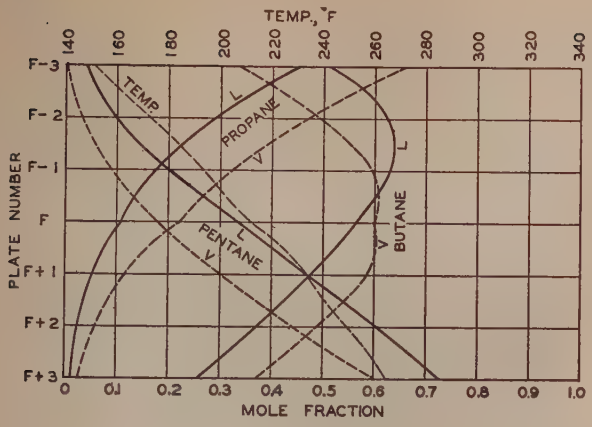
TEMP., °F
140
160
180
200
220
240
260
280
300
320
340
F-3
F-2
F-1
F
F+1
F+2
F+3
PLATE NUMBER
TEMP
PROPANE
PENTANE
BUTANE
L
V
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MOLE FRACTION

FIG. 1

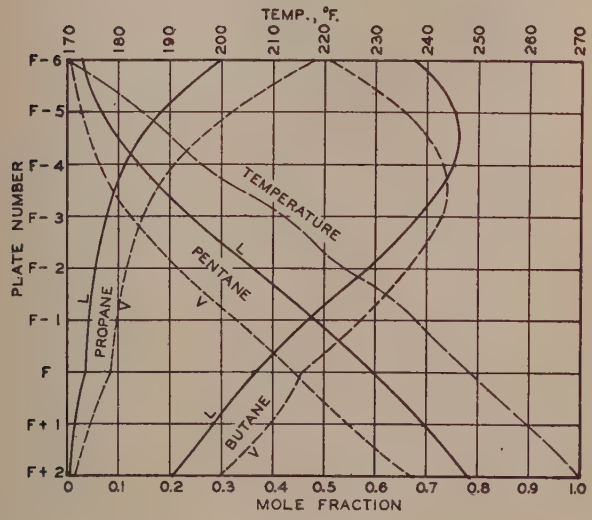
TEMP., °F.
170
180
190
200
210
220
230
240
250
260
270
F-6
F-5
F-4
F-3
F-2
F-1
F
F+1
F+2
PLATE NUMBER
TEMPERATURE
PENTANE
PROPANE
BUTANE
L
V
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MOLE FRACTION

FIG. 2

insofar as the composition of propane and butane in the distillate are concerned, but the composition of pentane varies widely.

In Column IV about 12.6 plates were used with practically the same propane-butane separation as with 11.1 or 10.5 plates in V and VI but the pentane content was greatly reduced by the excessive number of plates above the feed plate. In Column VI 10.5 plates were used with equivalent separation between propane and butane

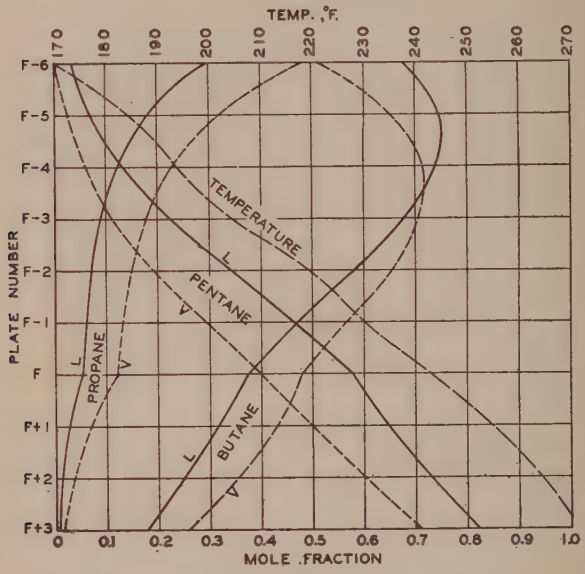

FIG. 3

and better pentane separation than in Column V which uses 11 plates.

The reason for these differences is in the location of the feed plate which must be properly located for best results. Because of the importance of proper location of the feed plate those methods of calculation which start with a determination of the feed plate offer more definite and satisfactory solutions.

Table VII gives a summary of results computed by the stepwise method in Tables I through VI, the results on a five-component mixture computed by Underwood,[75] and a comparison with results computed by means of the absorption factor method using the distillate

CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	.3000	.9599	.017186
Butane	.3500	.0400	.48286
Pentane	.3500	.0001	.499957
	1.0000	1.0000	1.000003

Function	Value
D	0.3
B	0.7
L	2.7
V	3.0
$\overline{L}$	3.7
$\overline{V}$	3.0
L/V	0.9
$\overline{L}/\overline{V}$	1.233
D/V	0.1
$B/\overline{V}$	0.233

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

Plate No.	Plate Temp.	"K"@ Plate Temp.	Plate Composition Mole Fraction Vapor	Plate Composition Mole Fraction Liquid	Compound
1	112°F.	1.045	.9740	.9310	Propane
		.405	.0279	.0690	Butane
		.151	.0000021	.0000138	Pentane
2	118°F.	1.10	.9340	.8485	Propane
		.435	.0660	.1515	Butane
		.166	.0000125	.0000756	Pentane
3	128°F.	1.20	.8600	.7170	Propane
		.495	.1400	.2825	Butane
		.194	.000068	.000352	Pentane
4	143°F.	1.35	.7410	.5485	Propane
		.58	.2585	.4455	Butane
		.24	.000317	.00132	Pentane
5	157°F.	1.50	.5900	.3930	Propane
		.67	.4050	.6040	Butane
		.29	.00119	.00408	Pentane
6	170°F.	1.63	.4500	.2780	Propane
		.77	.5470	.7130	Butane
		.34	.00367	.0108	Pentane
7	180°F.	1.72	.3460	.2011	Propane
		.84	.6460	.7690	Butane
		.375	.00971	.0259	Pentane
8	186°F.	1.775	.2770	.1560	Propane
		.885	.6960	.7870	Butane
		.405	.0233	.0575	Pentane
9	193°F.	1.84	.2365	.1284	Propane
		.94	.7125	.7585	Butane
		.44	.0518	.1178	Pentane
10 Feed	204°F.	1.94	.2115	.1089	Propane
		1.02	.6860	.6730	Butane
		.49	.1060	.2180	Pentane
11	215°F.	2.05	.1302	.0635	Propane
		1.10	.7172	.6520	Butane
		.545	.1527	.2800	Pentane
12	227°F.	2.14	.0743	.0347	Propane
		1.17	.6900	.5900	Butane
		.61	.2288	.3750	Pentane
13 Bottom	242°F.	2.26	.0388	.01716	Propane
		1.274	.6160	.48286	Butane
		.692	.3460	.49998	Pentane

CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	.3000	.9599	.017186
Butane	.3500	.0400	.48286
Pentane	.3500	.0001	.499957
	1.0000	1.0000	1.000003

Function	Value
D	0.3
B	0.7
L	2.7
V	3.0
$\overline{L}$	3.7
$\overline{V}$	3.0
L/V	0.9
$\overline{L}/\overline{V}$	1.233
D/V	0.1
$B/\overline{V}$	0.233

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

TABLE V

Plate No.	Plate Temp.	"K"@ Plate Temp.	Plate Composition, Mole Fraction, Vapor	Plate Composition, Mole Fraction, Liquid	Compound
1	110°F.	1.02	.9780	.9570	Propane
		.40	.0162	.0405	Butane
		.147	.00018	.00122	Pentane
2	118°F.	1.10	.9570	.9030	Propane
		.435	.0405	.0930	Butane
		.166	.00111	.0067	Pentane
3	124°F.	1.16	.9080	.7820	Propane
		.47	.0877	.1866	Butane
		.182	.00603	.0331	Pentane
4 Feed	144°F.	1.37	.8000	.5840	Propane
		.588	.1720	.2915	Butane
		.238	.0298	.1251	Pentane
5	154°F.	1.47	.7165	.4875	Propane
		.654	.2475	.3790	Butane
		.282	.0377	.1334	Pentane
6	166°F.	1.59	.5970	.3760	Propane
		.738	.3570	.4850	Butane
		.324	.0470	.1453	Pentane
7	180°F.	1.72	.4600	.2615	Propane
		.84	.4855	.5780	Butane
		.375	.0591	.1574	Pentane
8	191°F.	1.82	.3185	.1748	Propane
		.927	.6000	.6475	Butane
		.43	.0776	.1804	Pentane
9	204°F.	1.94	.2115	.1089	Propane
		1.02	.6860	.6730	Butane
		.49	.1060	.2180	Pentane
10	215°F.	2.05	.1302	.0635	Propane
		1.10	.7172	.6520	Butane
		.545	.1527	.2800	Pentane
11	227°F.	2.14	.0743	.0347	Propane
		1.17	.6900	.5900	Butane
		.61	.2288	.3750	Pentane
12 Bottom	242°F.	2.26	.0388	.01716	Propane
		1.274	.6160	.48286	Butane
		.692	.3460	.49998	Pentane

CONDITIONS FOR DESIGN

	Feed	Dist.	Bottoms
Propane	.3000	.9599	.017186
Butane	.3500	.0400	.48286
Pentane	.3500	.0001	.499957
	1.0000	1.0000	1.000003

Function	Value
D	0.3
B	0.7
L	2.7
V	3.0
$\overline{L}$	3.7
$\overline{V}$	3.0
L/V	0.9
$\overline{L}/\overline{V}$	1.233
D/V	0.1
$B/\overline{V}$	0.233

NOTE: Feed is all liquid and at temperature of feed plate. Pressure, 200 lbs. per sq. in. absolute.

TABLE VI

Plate No.	Plate Temp.	"K"@ Plate Temp.	Plate Composition, Mole Fraction, Vapor	Plate Composition, Mole Fraction, Liquid	Compound
1	111°F.	1.04	.9770	.9400	Propane
		.40	.02375	.0594	Butane
		.149	.0000823	.000552	Pentane
2	117°F.	1.09	.9415	.8645	Propane
		.43	.0574	.1333	Butane
		.163	.000491	.00301	Pentane
3	127°F.	1.19	.8740	.7344	Propane
		.485	.1240	.2514	Butane
		.19	.00271	.01427	Pentane
4	144°F.	1.36	.7568	.5560	Propane
		.588	.2304	.3920	Butane
		.246	.01284	.0522	Pentane
5 Feed	166°F.	1.59	.5970	.3760	Propane
		.738	.3570	.4850	Butane
		.324	.0470	.1453	Pentane
6	180°F.	1.72	.4600	.2615	Propane
		.84	.4855	.5780	Butane
		.375	.0591	.1574	Pentane
7	191°F.	1.82	.3185	.1748	Propane
		.927	.6000	.6475	Butane
		.430	.0776	.1804	Pentane
8	204°F.	1.94	.2115	.1089	Propane
		1.02	.6860	.6730	Butane
		.49	.1060	.2180	Pentane
9	215°F.	2.05	.1302	.0635	Propane
		1.10	.7172	.6520	Butane
		.545	.1527	.2800	Pentane
10	227°F.	2.14	.0743	.0347	Propane
		1.17	.6900	.5900	Butane
		.61	.2288	.3750	Pentane
11 Bottom	242°F.	2.26	.0388	.01716	Propane
		1.274	.6160	.48286	Butane
		.692	.3460	.49998	Pentane

and bottoms as the terminal conditions. Clearly the simpler absorption factor method is as reliable as the laborious stepwise calculations under the rather wide range of conditions covered in these calculations.

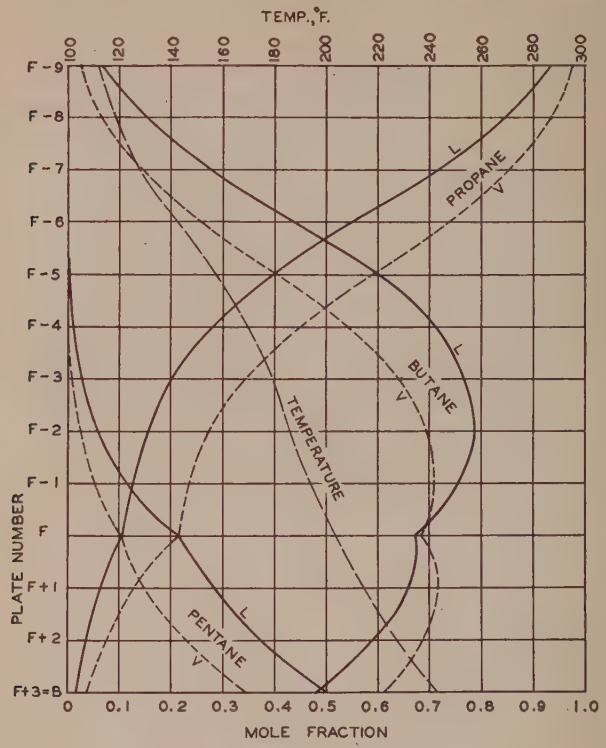

FIG. 4

The application of the absorption factor method to the conditions used in calculating Column VI will serve as an example of the method.

Assuming the temperature of the feed plate to be 166°F. and applying Equation (14) to n-pentane,

$$x_{c_f} = \frac{\frac{B}{\bar{V}} x_{c_B}}{\frac{\bar{L}}{\bar{V}} - K_{c_f}} \qquad (14)$$

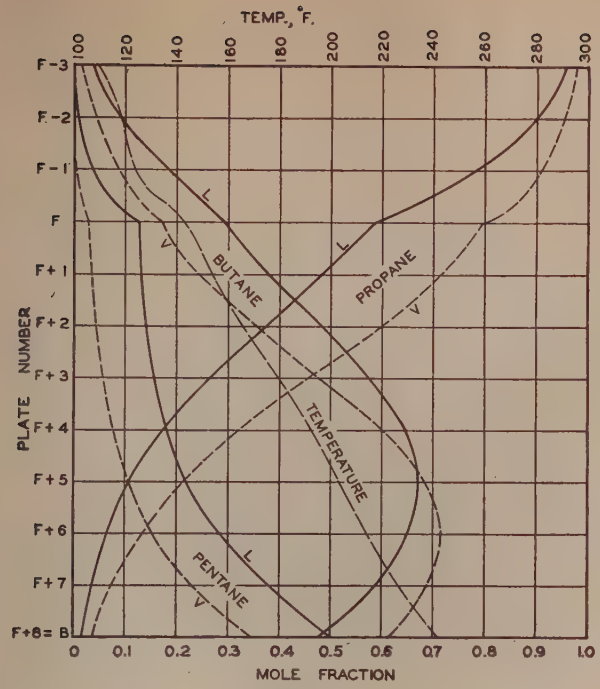
TEMP., °F.
100
120
140
160
180
200
220
240
260
280
300
F-3
F-2
F-1
F
F+1
F+2
F+3
F+4
F+5
F+6
F+7
F+8= B
PLATE NUMBER
L
V
BUTANE
PROPANE
TEMPERATURE
PENTANE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MOLE FRACTION

FIG. 5

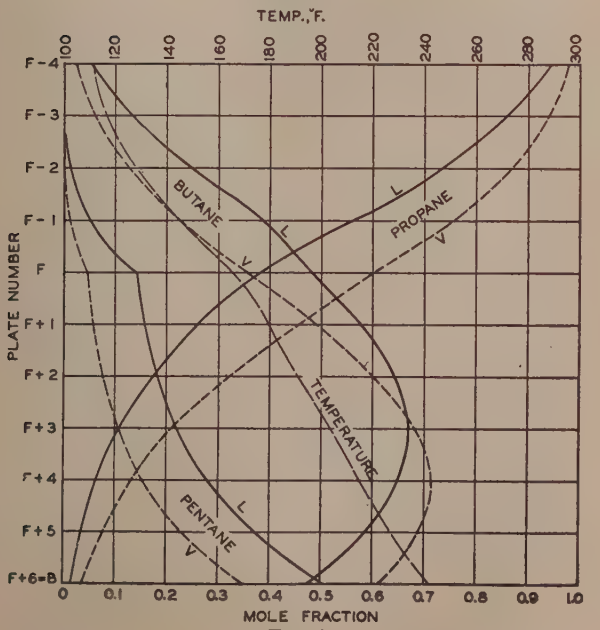
TEMP.,°F.
100
120
140
160
180
200
220
240
260
280
300
F-4
F-3
F-2
F-1
F
F+1
F+2
F+3
F+4
F+5
F+6=B
PLATE NUMBER
L
V
BUTANE
PROPANE
TEMPERATURE
PENTANE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MOLE FRACTION

FIG. 6

$$x_{c_f} = \frac{0.233 \times 0.5}{1.233 - 0.324} = 0.1281$$

$$x_a + x_b = 1 - x_c$$

$$x_{a_f} + x_{b_f} = 0.8719$$

$$K_a\, x_a + K_b x_b = 1 - K_c\, x_c$$

$$1.59\, x_{a_f} + 0.738\, x_{b_f} = 1 - 0.324 \times 0.1281$$

$$x_{b_f} = 0.5022$$

$$x_{a_f} = 0.3697$$

$$y_{b_f} = 0.3706$$

Applying the absorption factor to n-butane above the feed plate,

$$t_t = 118°\ \text{F.};\quad K_t = 0.435$$

$$t_{f-1} = 153°\ \text{F.};\quad \frac{K_{f-1} = 0.64}{K_A = 0.537}$$

$$A = \frac{L}{K_A V} = \frac{0.9}{0.537} = 1.67$$

$$\frac{y_f - y_D}{y_f - K_1 x_D} = \frac{0.3706 - 0.04}{0.3706 - 0.435 \times 0.04} = 0.935$$

From Equation (20) (plotted in Fig. 7) 3.8 theoretical plates are required above the feed plate.

Applying the stripping factor to propane below the feed plate,

$$t_{f+1} = 179°\ \text{F.};\quad K_{f+1} = 1.69$$

$$t_b = 242°\ \text{F.};\quad \frac{K_b = 2.29}{K_S = 1.99}$$

$$S = \frac{K_S \bar{V}}{\bar{L}} = \frac{1.99}{1.233} = 1.614$$

$$\frac{x_f - x_B}{x_f - \frac{x_B}{K_B}} = \frac{0.3697 - 0.01719}{0.3697 - \frac{0.01719}{2.29}} = 0.973$$

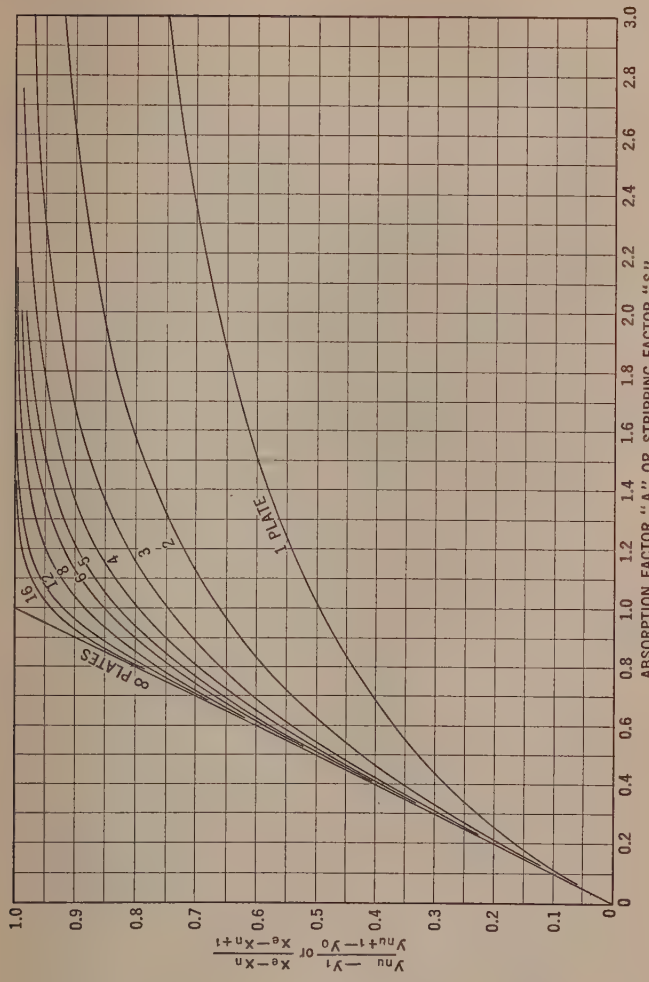
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0
ABSORPTION FACTOR "A" OR STRIPPING FACTOR "S"
$\frac{y_{nu} - y_1}{y_{nu+1} - y_0}$ or $\frac{x_e - x_n}{x_e - x_{n+1}}$
1 PLATE
2
3
4
5-6
7-8
12
19
∞ PLATES

FIG. 7

From Equation (22) (plotted in Fig. 7) 5.7 theoretical plates are required below the feed plate.

Checking the assumed temperature of the feed plate (166°F.)

$$t_f = 118 + \frac{3.8}{9.5}\ (242 - 118) = 167°\ \text{F.}$$

If the composition on the feed plate as determined by stepwise calculation is used with the absorption factor method the same results are obtained (except IV) as when the calculations are made by the stepwise method. This fact indicates that errors in the number of plates as determined by the absorption factor method arise in the calculation of the feed plate composition based on the two assumptions (1) linear temperature distribution and (2) Equations (13) and (14), rather than from the use of average equilibrium constants.

The application of the absorption factor in the same manner to pentane in columns IV, V and VI checks the number of plates in the rectifying section as calculated by the stepwise method even better than the application to butane (the less volatile cut-component). In column six this calculation indicates 3.4 + plates compared with 3.5 plates by the stepwise calculation. This indicates that the number of plates required in the rectifying column may be determined by the absorption factor as applied to any of the less volatile components whose composition in the distillate is significant.

If the number of plates above and below the feed plate have been determined by applying the absorption and stripping factors respectively to the least volatile and most volatile distributed components, Equations (20) or (22) may also be used to calculate the small concentrations in the distillate or bottoms of components which initially were assumed to be absent from these products.

The comparative results given in Table VII between the absorption factor method, and the stepwise plate-to-plate calculations of the number of equilibrium plates required in a fractionating column, indicate that, within the error of stepwise calculation (about one-half an equilibrium plate), the same results are obtained as to composition of distillate and bottoms, reflux ratio, and the number of equilibrium plates required above and below the feed plate. The examples cover a range of conditions and appear to justify the use of the convenient absorption factor procedure in place of the more tedious plate-to-plate calculation, except when the composition on every plate is desired.

The proper location of the feed plate can be determined only by

TABLE VII

Column Number	Component	Feed Mole Fraction	Distillate			Bottoms			Feed Plate				D/F	L/V	Number of Equilibrium Plates					
									Mole Fraction						Above Feed Plate n		Below Feed		Total No. of plates n + m + 1	
			Mole Fraction	Temp. ° F.	"K"	Mole Fraction	Temp. ° F.	"K"	Stepwise Calculation	Absorption Factor	Temp. ° F.	"K"			Stepwise Calculation	Absorption Factor	Stepwise Calculation	Absorption Factor	Stepwise Calculation	Absorption Factor
I	Propane	.3333	.6567	153	1.46	.0100	258	2.41	.109	.0586	212	2.02	0.5	0.9	3	2.6	2.87	2.3	6.87	5.9
	Butane	.3333	.3333		.65	.3333		1.38	.560	.709		1.07								
	Pentane	.3333	.0100		.28	.6567		.788	.331	.2324		.53								
II	Propane	.1500	.47667	170	1.62	.0100	269	2.51	.0373	.0334	248	2.33	0.3	0.9	6	6	1.78	1.6	8.78	8.6
	Butane	.3000	.51333		.76	.20857		1.45	.3628	.3676		1.30								
	Pentane	.5500	.0100		.334	.78143		.86	.5999	.5990		.74								
III	Propane	.1500	.47667	170	1.62	.0100	269	2.51	.0520	.0500	243	2.28	0.3	0.85	6	6	2.5	2.4	9.5	9.4
	Butane	.3000	.51333		.76	.2086		1.45	.3740	.3670		1.285								
	Pentane	.5500	.0100		.334	.7814		.86	.5740	.5830		.698								
IV	Propane	.3000	.9599	118	1.10	.01719	242	2.29	.1089	.0936	204	1.94	0.3	0.9	8.6	8.0	3	2.7	12.6	11.7
	Butane	.3500	.0400		.435	.48286		1.274	.6730	.7058		1.02								
	Pentane	.3500	.000008		.166	.49995		.692	.2180	.201		.49								
V	Propane	.3000	.9599	118	1.10	.01719	242	2.29	.5840	.563	144	1.37	0.3	0.9	2.1	2.2	8	7.4	11.1	10.6
	Butane	.3500	.0400		.435	.48286		1.274	.2910	.320		.588								
	Pentane	.3500	.00102		.166	.49995		.692	.1250	.117		.238								
VI	Propane	.3000	.9599	118	1.10	.01719	242	2.29	.3736	.3697	166	1.59	0.3	0.9	3.5	3.8	6	5.7	10.5	10.5
	Butane	.3500	.0400		.435	.48286		2.274	.4820	.5022		.738								
	Pentane	.3500	.00023		.166	.49995		.692	.1444	.1281		.324								
VII	Hexane	.310	.536	187.9	.....	.....	285.3	.....	.068	.0624	224.4	2.9	0.5777	.75	6	5.6	10	10.3	17	16.9
	Heptane	.266	.46		.....	.00134		3.0	.422	.4602		1.29								
	Octane	.187	.00406		.29	.437		.....	.368	.3480		0.566								
	Nonane	.125	.....		.....	.296		.....	.082	.0726		.275								
	Decane	.112	.....		.....	266		.....	.060	.0564		.135								

NOTE: Feed to columns I—VI considered as all liquid and at temperature of feed plate.
Pressure 200 lbs. per sq. in. absolute. Feed plate compositions are for liquid on plate.
Feed to column VII half vapor and half liquid. Pressure atmospheric. Equilibrium determined by Raoult's Law, K = p/P.

a cut and try procedure when using the stepwise calculation as applied to the first six examples, but the effect of the location of the feed plate on the composition of the distillate and bottoms is clearly brought out. If the location of the feed plate is determined by the relationship given in Equation (18) as developed by Underwood,[75] the proper location of the feed plate will be determined for the efficient separation between two adjacent components, b and c. In cases where a sharp separation between two adjacent components is desired this method is entirely adequate and satisfactory. But a change in the location of the feed plate from the proper location so determined may have a pronounced effect on the composition of the distillate in terms of the other components, which may be desired under some conditions.

The importance of the location of the feed plate is clearly brought out by comparing the computed results in columns IV, V, and VI in Table VII. Substantially the same separation between propane and butane is accomplished in each of these columns, but the composition of pentane in the distillate changes one hundred fold, from 0.1% to 0.0008% as the feed plate is dropped from the 9th plate above the bottom to the 4th plate above the bottom and about one and a half equilibrium plates are added to the top of the column. The compositions of the bottoms in each case are identical.

Comparison between computed columns V and VI in Table VII is perhaps even more interesting as here we have obtained an improvement in the rectification of pentane in the distillate with no sacrifice, but rather an improvement, in the fractionation between propane and butane by dropping the feed plate two equilibrium plates. Furthermore the better rectification of pentane is obtained in column VI which is indicated as having one-half an equilibrium plate less than column V.

Proper location of the feed plate is an important consideration which may not be overlooked if best results are to be obtained. But it is necessary that the designer have clearly in mind the most desirable characteristics to be obtained in the products of the fractional distillation before the proper location of the feed plate may be accurately determined. As has been indicated the relationship given in Equation (18) is most satisfactory when a sharp separation between two adjacent components is the purpose of the column. Fortunately this is frequently the object of fractional distillation and Equation

(18) offers an adequate solution. But in many cases where it may be desired to obtain a definite ratio between two adjacent components with a minimum of a third component, the relationship given in Equation (18) may be misleading. This special case is frequently encountered in the gasoline industry when it is desired to prepare a stable gasoline of limited vapor pressure from a feed which may contain an excess of butane. Under such conditions it is desired to lose a minimum quantity of pentane in the distillate, and to retain a minimum quantity of isobutane in the bottoms. On this basis alone it would appear that the problem might be treated as one requiring the separation between isobutane and isopentane, but with the normal butane in the bottom product limited to a definite percentage by the specification for vapor pressure. If separation between iso and normal butane is used as the basis of calculation, excessive loss of isopentane is likely to occur.

It has been suggested in the first part of this paper that such a problem be treated as a fractionating column with three components distributed in both distillate and bottoms. Columns I, II and III represent such problems and Table VII indicates that the absorption factor method arrives at an adequate solution. Even in Column I, which is an extreme case for which the calculation of the composition at the feed plate is unsatisfactory, the absorption factor method yields results which are adequate for most engineering purposes.

A study of the results reported in Table VII clearly indicates the sources of errors, or disagreements between the stepwise calculation and the absorption factor method. In the first column (I) the estimated feed plate composition for propane is in error by almost 50 per cent and the error in the number of plates required in the stripping section to strip the propane from the estimated feed plate composition is 20 per cent. This error is the greatest indicated error in the absorption factor method as compared with the rigorous plate to plate computation, and is due entirely to error in the estimated feed plate composition.

In all other cases the feed plate composition as estimated by the absorption factor method agrees fairly well, within about 10 per cent, with the composition of the feed plate as computed from the stepwise calculations. In columns II and III, all three components are present in appreciable quantities in both the overhead and the bottoms, and the estimated composition of the feed plate is not as satisfactory as in

columns V and VI where a sharp separation is being made between two adjacent components.

Volume IV (Figure 4) is of particular interest as it is the only column included in Table VII in which one of the cut components goes through a distinct maximum between the terminal plates. By referring to Figure 4 or Table IV, it is seen that the mole fraction of butane on the feed plate is 0.673. It increases to a maximum of 0.787 two plates above and then decreases to 0.069 on the top plates. In applying the absorption factor method to the absorption of butane in the rectifying section of column IV, it was assumed that the average effective value for the equilibrium constant of butane in the rectifying column could be estimated as the arithmetric average of the values of the equilibrium constants on the top plate, and the plate above the feed plate. This introduces an error in the number of plates required in the rectifying part of the column, which in turn introduces an error in the composition of butane on the feed plate. In this case one error tends to compensate for the other. The composition of butane on the feed plate is almost 5 per cent too high and the number of equilibrium plates estimated for the rectifying column is almost 7 per cent too low. These results indicate an error of about 12 per cent in the application of the absorption factor itself to butane which goes through a maximum in the rectifying section of this column. In order to check this indication, the number of equilibrium plates in the rectifying section of the column was computed using as the composition of butane on the feed plate 0.673, or 0.6865 mole fraction of butane in the vapor rising into the rectifying section of the column. The results of this calculation indicated that 7.5 equilibrium plates would be required to reduce the butane content in the overhead to a mole fraction of 0.04. This figure is too low by 1.1 equilibrium plates and indicates an error of 12.8 per cent due to the assumption that the average effective equilibrium constant may be taken as the arithmetric mean when the component goes through a maximum composition between the terminal plates.

If the maximum in the composition of the component to which the absorption factor is applied is more pronounced, it would be expected that a greater error would be introduced. In columns I, II, and III it will be observed that the butane goes through a maximum in each case in the rectifying section, but in the calculation of these columns the absorption factor method is applied to pentane in the rectifying

section and not to the butane, with satisfactory results in all cases. The error in the case of column I was due to an error in the estimated feed plate composition.

CONCLUSIONS

This comparison of the absorption factor method with the rigorous stepwise calculation indicates that there are two sources of possible error in the application of the absorption factor method as described.

1. Errors in the estimated composition of the feed plate.
2. Errors introduced by applying an arithmetric average for the value of the equilibrium constant, K, to a component which goes through a maximum composition between the terminal plates.

If the column is making a sharp separation between two adjacent components and the feed plate is so located as to accomplish this separation in the most efficient manner, the estimated composition of the feed plate is substantially correct and none of the cut components go through a maximum in that part of the column where the absorption factor method would be applied, and the method as outlined may be used with satisfactory results.

If there are to be three distributed components present in appreciable quantities in both the overhead and the bottoms, as in the case of columns I, II and III, the estimated composition of the feed plate may be in considerable error unless the ratio of plates above the feed plate to the plates below the feed plate is two or more. In any column in which one component is distributed between the overhead and the bottoms, that is, not reduced to a minimum in either the overhead or the bottom, the component so distributed is very likely to go through a maximum at some point between the terminal plates. Therefore it is necessary to apply the absorption factor method to another component which is not so distributed, but is reduced to a minimum in either the overhead or the bottoms as the case may be, in order to obtain reliable results. This was done in columns I, II and III by applying the absorption factor method to propane in the stripping section and pentane in the rectifying section.

In many columns that are apparently making a sharp separation between two adjacent components, the feed plate may be so located that in effect the column is actually distributing one intermediate component between the top and the bottom. In such a case reliable results can be obtained only by applying the absorption factor method to

another component which is not distributed. This type of operation is exemplified by column IV in Table VII in which the composition of the tops and bottoms in respect to propane and butane are the same as in columns V and VI. But due to the peculiar location of the feed plate in column IV the column is operating as though it were distributing butane between the overhead and the bottoms. The butane goes through a maximum in the rectifying part of the column and the correct number of plates can be obtained only by applying the absorption factor method to pentane in the rectifying part of the column.

If these difficulties, the equivalent of which are common to most methods, are kept in mind, the absorption factor methods as outlined should prove a convenient fairly reliable procedure for the design or calculation of the number of equilibrium plates required for the separation of complex mixtures, provided equilibrium may be expressed in terms of an equilibrium constant as for ideal solutions.

FRACTIONAL DISTILLATION

III. Application of Theoretical Method of Calculation to Commercial Gasoline Stabilizer Test Data

By E. G. RAGATZ,* H. V. NYLAND,† MOTT SOUDERS, JR.,† and GEORGE GRANGER BROWN †

The greatest difficulty in attempting to check theoretical methods for the calculation of the number of plates required in a fractionating column, against actual operating data, is that of obtaining sufficiently complete and reliable data on the commercial plant. If simply the feed, overhead distillate, and bottoms are known as to quantity and quality, it is impossible to determine the actual operating efficiency of the plates in the column and therefore impossible to determine the equivalent number of equilibrium plates actually required to effect the separation.

Test Data

The test data used in this comparison include not only these essential data but also the complete analysis of the liquid samples as withdrawn from 17 of the 48 plates. Fig. 8 is a simplified flow diagram of the gasoline stabilizer, with the quantity of all significant streams indicated. Table VIII gives the composition of feed, bottoms, distillate, reflux, side-cut and liquid on various plates with the corresponding temperatures. Fig. 9 shows the temperature distribution in the column with all actual measurements indicated. The dotted line is an estimate of the temperature of the vapor at the top of the column based upon a single temperature reading of 130°F. for the vapors above the top tray. The important point is the effect of cold liquid reflux on the temperature of the liquid at the top of the column rather than the exact number of plates required for substantial equalization of the temperatures of the liquids and vapors.

In Fig. 10 the composition of the liquid plate samples is plotted in such a manner that the mole fraction of any one component is the difference between the values given between two points. This means

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that the mole fraction of any one component on any plate is represented by the difference between two lines rather than the value of a particular line. The areas formed between these lines are labelled

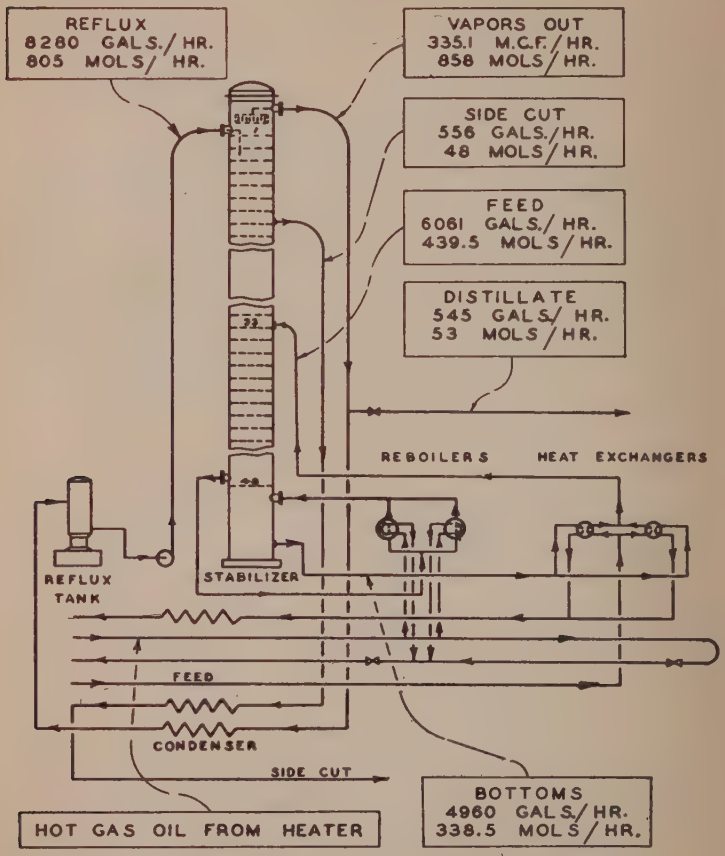

FIG. 8

with the name of the corresponding component. The lines drawn through the points represent the levelled data which has been used in the following computation. Except for the separation between iso and normal butane, and between iso and normal pentane in a few

samples from plates in the lower part of the column, the data appear unusually consistent and reliable.

In Fig. 11 the composition of the vapor rising from the plate is plotted in a similar manner, the circles indicating the vapor composi-

TABLE VIII. TEST DATA FOR GASOLINE STABILIZER

	Feed	Bottoms	Distillate	Reflux	Distillate plus side cut	Trays Below Feed 46	44	42	40	36
CH_4 (mol fraction)	0.0029		0.0258		0.0135					
C_2H_6	0.0382		0.1335		0.0732					
C_3H_8	0.1226		0.782		0.5875			0.0014	0.0052	.0239
iso—C_4H_{10}	0.0798	0.0347	0.0527		0.2900	.0907	.0874	0.0966	0.1489	.1577
n—C_4H_{10}	0.2752	0.3295	0.0035		0.0357	.5731	.6311	0.662	0.5867	.5452
iso—C_5H_{12}	0.103	0.1303	0.0025(?)			.1051	.0944	0.0743	0.078	.0699
n—C_5H_{12}	0 0929	0.1125				.0821	.0631	0.0277	0.0573	.0611
C_7H_{16}	0.2854	0.393				.149	.124	0.138	0.1239	.1422
Reflux Ratio										
$\left(\frac{L}{D}\right)$										
$\left(\frac{L}{V}\right)$						1.32		1.325		1.33
Quantity (mols/hr.)	439.5	338.5	53	805	101					
Temperature (°F.)	255	330	130	72		278	272	268	266	262
Trays								15		

Trays Above Feed

	32	30	24	22	20	16	14	12	10	Side-cut 6	4	2
CH_4 (mol fraction)											0.0180	0.0184
C_2H_6	.0054	.009	.0022	.0012	.0029	.0032	.0021	.0016	0.003	0.0033	0.0243	0.1053
C_3H_8	.0902	.0839	.0897	.0898	.0905	.0889	.1026	.0857	0.1204	0.3697	0.780	0.8085
iso—C_4H_{10}	.195	.2514	.264	.3042	.3586	.4365	.4794	.5408	0.5896	0.5524	0.1774	0.0638
n—C_4H_{10}	.5744	.6192	.6403	.6036	.5449	.4694	.4124	.3688	0.287	0.0713	0.0165	0.004
iso—C_5H_{12}	.0536	.0214	.0038	.0012	.0031	.002	.0035	.0031		0.0053		
n—C_5H_{12}	.0375	.0106										
C_7H_{16}	.0439	.0045										
Reflux Ratio												
$\left(\frac{L}{D}\right)$	8.06	9.35	9.45	9.45	9.45	.945	9.45	9.45	9.45		19.2	16.6
$\left(\frac{L}{V}\right)$	.89	.903	.905	.905	.905	.905	9.05	.905	0.905		0.95	0.943
Quantity (mols/hr.)												
Temperature (°F.)	235	225	221	220	219	217	216	213	209	184	161	116
Trays					32							

tion as computed from actual liquid analysis by means of equilibrium relationships based upon ideal solutions, and the triangular points represent the composition of the vapor as computed from heat and material balances around parts of the column. The lines represent

the levelled data as in the case of Fig. 10. Comparison of the vapor composition as computed by the two different methods indicates that

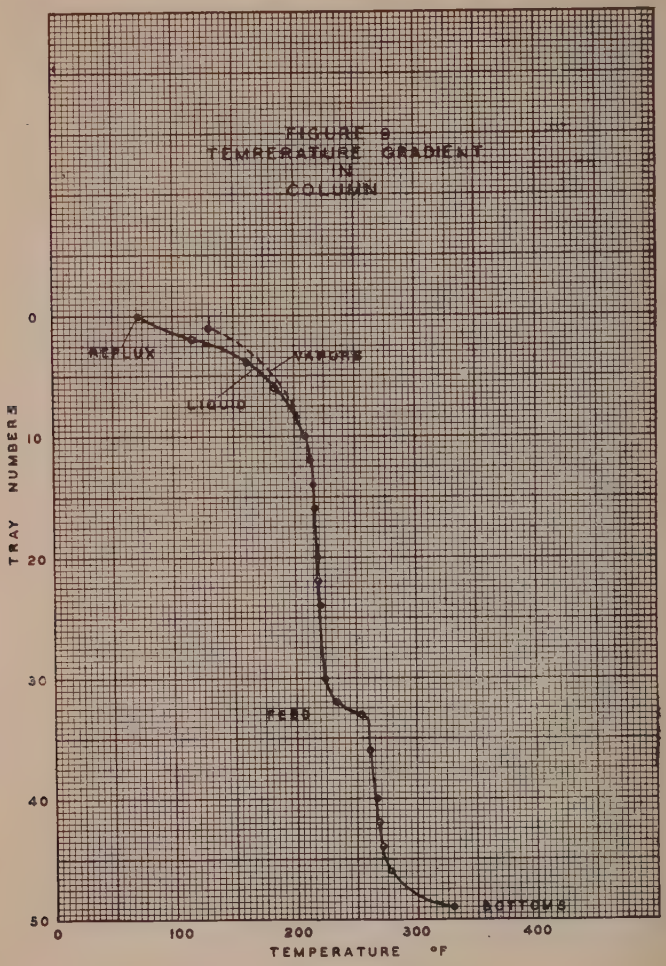

FIG. 9

the composition of the vapor as determined by heat and material balances is substantially the same as that computed from equilibrium data and the composition of the liquid. Therefore the plate efficiency

in this column under these conditions of operation is very close to 100%. In other words each actual plate is just about as effective as an equilibrium plate.

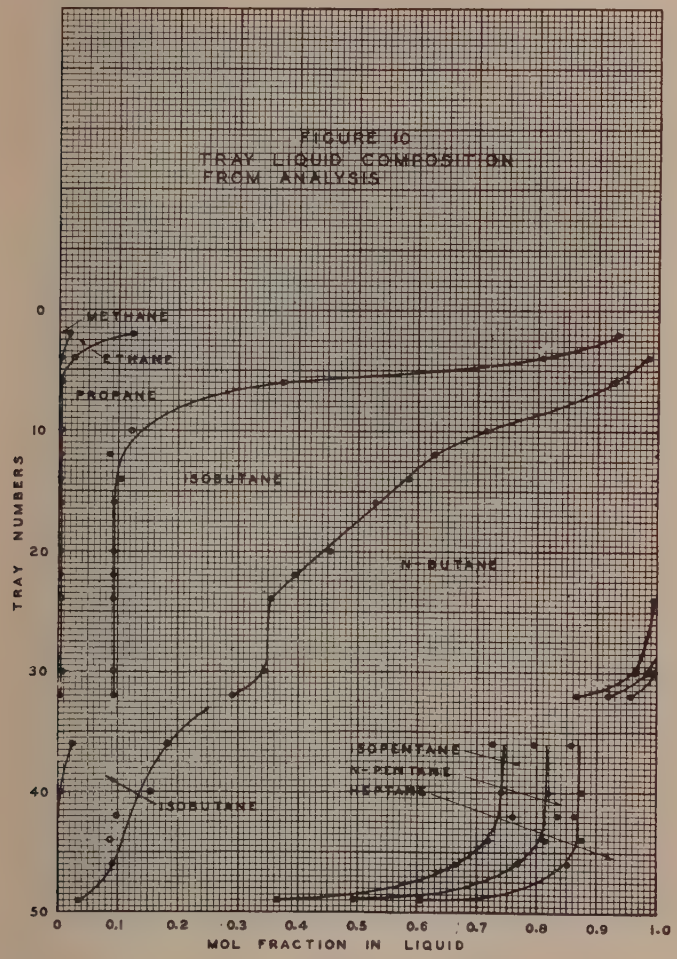

FIG. 10

In Fig. 12 the liquid overflow (L) in moles per hour is plotted for the various plates in the column. The ratio of liquid overflow to

vapor rising in the column (L/V) as calculated for various parts of the column is given in Table VIII and is practically constant in the

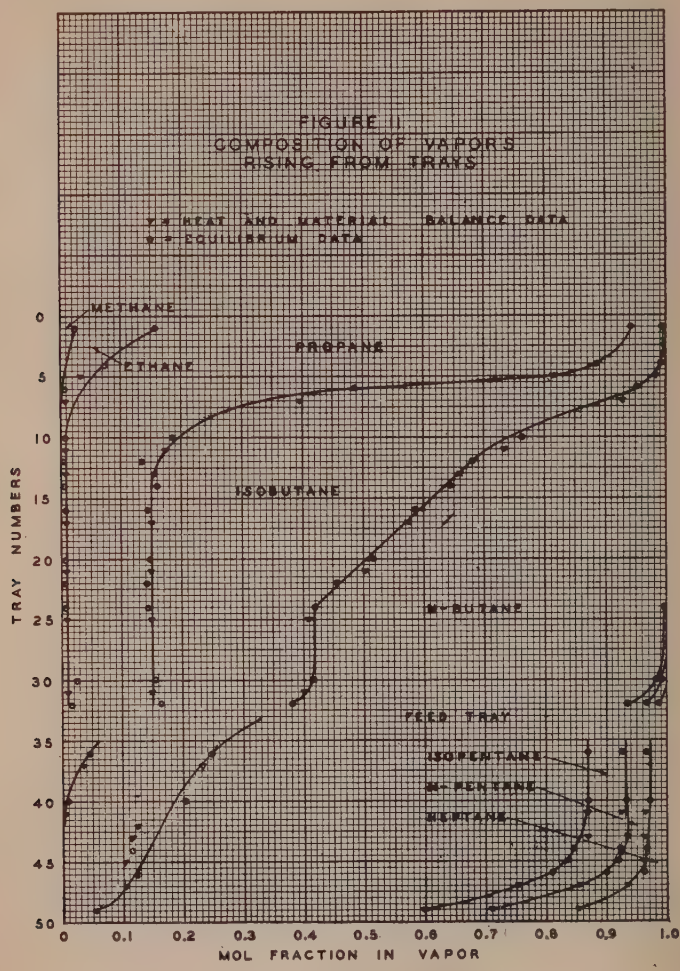

FIG. 11

stripping section (plate 34 to 48) and in the rectifying section below the side-stream (plate 7 through 32), with the exception of the

difference immediately above and below the feed plate. Above the side-cut the disturbing effect of the cold reflux is clearly evident.

Actual Individual Plate Efficiency

The most generally accepted definition of plate efficiency is that given by Murphree [52] and represented by the equation,

$$E_y = \frac{y_n - y_{n+1}}{y^*_n - y_{n+1}} = \frac{y_n - y_{n+1}}{K_n x_n - y_{n+1}} \qquad (25)$$

where

y_n = mol fraction of a component in vapors rising from a plate.

y_{n+1} = mol fraction of the component in vapors rising to the plate.

y^*_n = mol fraction of the component in vapors in equilibrium with the liquid leaving the plate = $K_n x_n$.

Similarly, the same plate efficiency defined in terms of the change in liquid compositions is represented by the equation,

$$E_x = \frac{x_{n-1} - x_n}{K_n \frac{V}{L} x_n - \frac{D}{L} x_D - x_n} \text{ or } \frac{x_{m-1} - x_m}{K_m \frac{\bar{V}}{\bar{L}} x_m + \frac{B}{\bar{L}} x_B - x_m} \qquad (26)$$

Other definitions have been used and frequently erroneously assumed to be identical with Equation (25) or (26), such as,

$$\frac{x_{n-1} - x_n}{x_{n-1} - x^*_n} = \frac{x_{n-1} - x_n}{x_{n-1} - \frac{y_n}{K_n}}$$

where

x_n = mol fraction of a component in liquid leaving a plate.

x_{n-1} = mol fraction of the component in liquid entering the plate.

x^*_n = mol fraction of the component in liquid in equilibrium with the vapors rising from the plate.

TABLE IX. INDIVIDUAL PLATE EFFICIENCIES (MURPHREE'S)

L/V = .905 L/D = 9.45	Plate 12 (214° F.)			Plate 15 (216° F.)		Plate 20 (218° F.)		Plate 32 (233° F.)	
	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}
x_{n-1}	.12	.545	.335	.483	.420	.370	.537	.220	.605
x_n	.107	.521	.372	.462	.444	.347	.560	.197	.573
x_D	.5875	.290	.0357						
D/Lx_D	.0622	.0307	.00378						
$D/L\,x_D + x_n$	.169	.552	.376	.493	.448	.378	.564	.228	.577
$x_{n-1} - x_n$	+.013	+.024	−.037	+.024	−.024	+.023	−.023	+.023	+.032
Equilibrium Constants (K) [67]									
K_n	1.5	.99	.85	1.00	.865	1.02	.88	1.11	.95
$K_nV/L\,x_n$	.177	.57	.349	.511	.425	.392	.545	.242	.601
Equilib. Plate									
$x_{n-1} - x_n$	+.008	+.018	−.027	+.018	−.023	+.014	− 019	+.014	+.024
E_x	1.62	1.33	1.37	1.33	1.04	1.64	1.21	1.64	1.33
K corrected: or Deviation from Ideal Solution									
A	1.14	1.047	1.068	1.056	1.057	1.073	1.042	1.105	1.04
$AK_nV/L\,x_n$	.202	.595	.372	.54	.449	.42	.568	.267	.624
Equilib. Plate									
$x_{n-1} - x_n$	+.033	.043	−.004	+.047	+.001	.042	+.004	.039	+.047
E_x	.394	.557	9.	.51	−24.00	.55	−5.75	.59	.68

TABLE IX. INDIVIDUAL PLATE EFFICIENCIES (MURPHREE'S)

$\bar{L}/V = 1.325$ $\bar{L}/B = 4.08$	Plate 46 (278°F.)			Plate 41 (266°F.)		Plate 40 (264°F.)		Plate 35 (260°F.)	
	iC_5H_{12}	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}	iC_4H_{10}	nC_4H_{10}
x_{m-1}	.092	.098	.597	.129	.606	.136	.598	.172	.520
x_m	.1051	.0907	.5731	.126	.613	.129	.606	.165	.541
x_B	.1303	.0347	.3295						
$B/\bar{L}\ x_B$	.0319	.00851	.0809						
$B/\bar{L}\ x_B - x_m$	−.0732	.0822	−.4922	−.1175	−.532	−.1285	−.525	−.1565	−.460
$x_{m-1} - x_m$	−.0131	+.0073	+.024	+.003	−.007	+.007	−.008	+.007	−.021
Equilibrium Constants (K) [67]									
K_m	.83	1.31	1.17	1.27	1.11	1.25	1.10	1.22	1.08
$K_m(\bar{V}/\bar{L})x_m$	.0659	.0898	.5062	.1208	.514	+.1178	.504	.152	.441
Equilib. Plate									
$x_{m-1} - x_m$	−.0073	+.0075	+.014	+.0033	−.018	+.0107	−.021	−.0045	−.019
E_x	1.79	0.973	1.71	.91	.39	.655	.38	1.67	1.11

Any effort at defining individual plate efficiency must be arbitrary, but usage and logic are both in support of E_y or E_x as defined in Equations (25) and (26). In commercial work the overall plate efficiency, defined as the ratio of the number of equilibrium plates to number of actual plates required for the same separation is of more practical value and can be determined with less error. As shown by Holbrook and Baker the overall plate efficiency may be more or less than the Murphree or individual plate efficiency, depending upon the nature of the equilibrium curve and operating line. The overall and individual plate efficiencies are equal only when the equilibrium curve and operating line are straight and parallel, or when the individual plate efficiency is unity.

For these reasons it is suggested that only two definitions of plate efficiency be accepted, Murphree's [52] individual plate efficiency as defined by Equations (25) and (26) and the overall plate efficiency defined as the number of equilibrium plates divided by the number of actual plates.

Individual plate efficiencies were calculated by Equation (26) from actual data given in Table VIII and interpolations thereof from Fig. 10. The individual plate efficiencies calculated in this manner are given in Table IX.

Plate efficiencies were calculated on the basis of the equilibrium constants [71] which have been used in all of the calculations in this paper, and also on the basis of the same equilibrium constants as corrected for deviations from ideal solutions according to the estimated correction factor of Katz and Brown.[33] The computation of the individual plate efficiencies by Equation (26) is a rather unsatisfactory procedure. Due to the fact that the efficiency is determined by subtracting two numbers of approximately the same order of magnitude, the method is extremely sensitive to errors in the data and errors in the equilibrium relationship.

Although the individual plate efficiency is of considerable theoretical significance, in the practical design and operation of commercial columns the overall or average plate efficiency is of much greater significance.

The individual plate efficiency as indicated in Table IX averages somewhat over 100%, and is relatively more consistent on plates above the feed plate and when the uncorrected equilibrium constants are used. Substantially the same results are indicated in Fig. 11 in

which the vapor in equilibrium with the liquid was computed by use of the uncorrected equilibrium constants.

As suggested by Katz and Brown,[33] the use of the corrections with the equilibrium constants is not justified in the computation of plate efficiency and the design of fractionating equipment, at least until more information is available concerning the deviation from ideal solutions. On the other hand the high plate efficiencies indicated in some cases when no correction factor is used, are without doubt fictitious as they are invariably greatly reduced when a correction factor is applied to the equilibrium constant.

Algebraic Method[44]

This column was analyzed, first of all, by attempting to work down from the given distillate composition and up from the given liquid composition on plate 46. Plate 46 was chosen as the starting point in preference to the bottoms because the liquid bottoms are not in equilibrium with the vapors rising into plate 48. The heating requirements are furnished by recirculating liquid from plate 48 through a heat exchanger, the vapors entering the column just below the plate. This arrangement upsets the equilibrium between liquid bottoms and vapors entering the bottom plate.

As an example of the calculations, a temperature is assumed for the liquid on plate 46, and the composition of the vapors in equilibrium with this liquid computed from the equilibrium constant (K) values at the assumed temperature and the pressure of the column. If Σy is unity the correct temperature has been assumed.

N-hexane and heavier components are considered as the single component, n-heptane.

	x_{46} mol fraction	K 283° F. (300 lbs. per sq. in. abs.)	y_{46} mol fraction
iso-C_4H_{10}	0.0907	1.34	0.1216
n-C_4H_{10}	0.5731	1.20	0.6875
iso-C_5H_{12}	0.1051	0.865	0.0910
n-C_5H_{12}	0.0821	0.76	0.0624
C_7H_{16}	0.1490	0.265	0.0394
	1.0000		1.0019

At a temperature of 283°F. the mol fractions in the vapors rising from plate 46 into plate 45 are now known. The composition of the

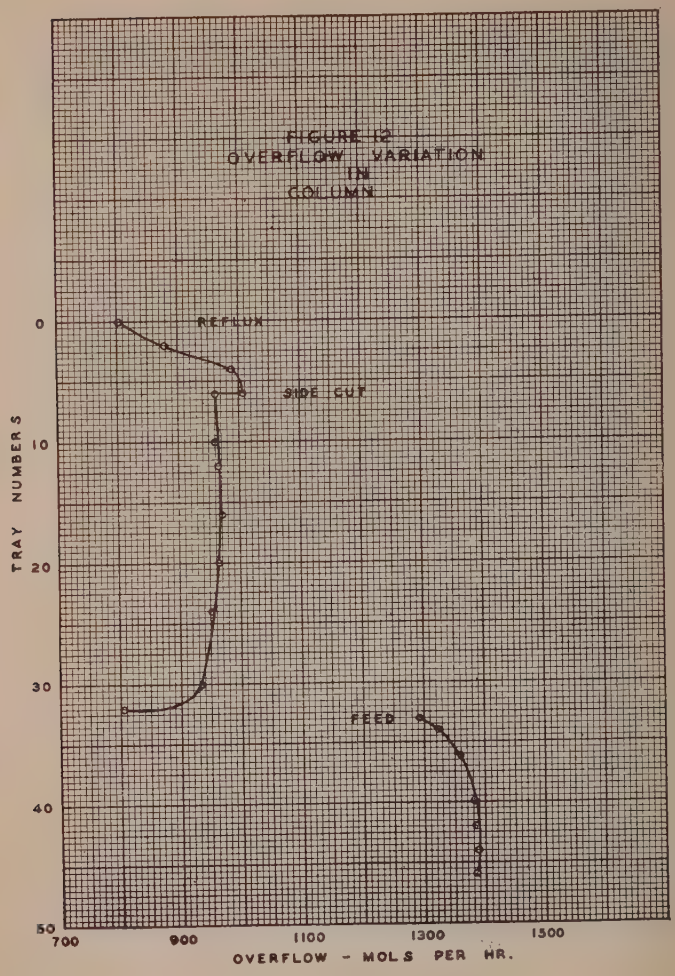
FIGURE 12
OVERFLOW VARIATION
IN
COLUMN
REFLUX
SIDE CUT
FEED
TRAY NUMBERS
0
10
20
30
40
50
700
900
1100
1300
1500
OVERFLOW - MOLS PER HR.

FIG. 12

liquid on plate 45 can then be calculated from a material balance using Equation (9):

$$x_{m-1} = \frac{\bar{V}}{\bar{L}} y_m + \frac{B}{\bar{L}} x_B$$

for

$$\text{iso-}C_4H_{10},\ x_{45} = 0.754\ (0.1216) + 0.246\ (0.0347) = 0.100$$
$$\text{n-}C_4H_{10},\ x_{45} = 0.754\ (0.6875) + 0.246\ (0.3295) = 0.5988$$
$$\text{iso-}C_5H_{12},\ x_{45} = 0.754\ (0.091) + 0.246\ (0.1303) = 0.1005$$
$$\text{n-}C_5H_{12},\ x_{45} = 0.754\ (0.0624) + 0.246\ (0.1125) = 0.0746$$
$$C_7H_{16},\ x_{45} = 0.754\ (0.0394) + 0.246\ (0.393) = 0.1261$$
$$1.000$$

No methane, ethane, or propane appears in the analysis of the liquid on plate 46. Therefore, some value must be assumed for these components in order that the calculations may be carried on to the feed plate with some degree of accuracy. A small amount of propane (0.14 per cent) was arbitrarily inserted in the liquid on plate 42 and the computations continued on up to the feed plate. Methane and ethane have a much smaller mol fraction in this section of the column and have been disregarded, although they also become of some importance in the vicinity of the feed plate.

Table X gives the results of the calculations which are plotted in Figures 13 and 14 with tray number as ordinates and mol fraction in the liquid as abscissae. The small triangles represent calculated values while the circles are experimental points.

The calculated curves agree fairly well with the experimental values, especially for the heavier components, indicating a plate efficiency of approximately 100%.

There is uncertainty, however, in the calculations of the upper part of the stripping column due to the more volatile components, methane, ethane and propane, the composition of which must be assumed.

Similar calculations were made for the rectifying section of the column, starting with the composition of vapors leaving the top of the column. Although 0.25 per cent of isopentane was reported in the distillate, there can be no measurable quantity of isopentane, pentane, or hexane present because none was found on plates 2 or 4. If 0.25 per cent of isopentane were present in the distillate, all of the

analyses of the upper plates would be in error. In the calculations no pentane was considered present until tray 21 was reached, at which small amounts of isopentane and n-pentane (0.02 per cent and 0.01 per cent respectively) were arbitrarily added to the liquid composition on that plate. The results of this effort are shown in Fig. 14 by the small triangles. For the upper part of the rectifying section where the less volatile components are absent and the uncertainty concerning them is removed, the calculated and experimental curves agree well for all components.

In the lower part of the rectifying column, where the less volatile components appear, the curves deviate due to the uncertainty in estimating the mol fractions of the less volatile constituents. The deviation of the computed from the observed compositions is even more pronounced in the dotted curves (Fig. 13) for isobutane and n-butane, which were calculated by introducing a greater quantity of isopentane (0.2 per cent at tray 15) and a greater quantity of n-pentane (0.1 per cent at tray 17). Heptane has been completely ignored, but it also would become of importance in the calculations near the feed plate.

When working from the top and bottom compositions toward the feed, no method is available by which the components less volatile than the heavy cut-component may be correctly incorporated into the computations of the rectifying section, and no means is known by which those components more volatile than the lighter cut-component may be correctly added to the calculations of the stripping section.

Efforts to estimate the composition on the feed plate by use of Equations (13) and (14) as has been suggested [44] were of little or no help in obtaining a satisfactory solution to the column calculations. Although practically the only method available for the complete calculation of columns from a theoretical standpoint, this method is not satisfactory for practical engineering work because of the large amount of calculation required and because of the relatively indefinite results obtained.

The Absorption Factor Method

In the second part of this study it was shown that the absorption factor method could be applied to the calculation of columns with substantially the same results as obtained from the more laborious plate-to-plate calculations. The following calculation gives the results obtained from applying the absorption factor method of calculation to an actual commercial gasoline stabilizer.

TABLE X. RESULTS OF ALGEBRAIC METHOD

MOL FRACTION IN LIQUID OR VAPOR

	y_1	x_1	y_2	x_2	y_3	x_3	y_4	x_4	y_5	x_5	y_6	x_6	y_7	x_7	y_8	x_8	y_9	x_9
Temp. (°F.)	133		146		155		163		172		182		188		197		202	
CH_4	0.0258	0.0021	0.00345	0.00026	0.0017	0.00012	0.00158	0.0001	0.00156	0.0000945	0.00154	.000087	0.0013	0.000067	0.00128	.000064	.00127	0.000058
C_2H_6	0.1335	0.069	0.0726	0.0356	0.0412	0.0195	0.026	0.0119	0.0188	0.00835	0.0755	.0066	0.0125	0.00515	0.0111	.0044	.0105	0.0041
C_3H_8	0.782	0.822	0.8196	0.788	0.7876	0.716	0.7196	0.623	0.6326	0.518	0.5331	.4185	0.434	0.324	0.348	.252	.283	0.20
iso—C_4H_{10}	0.0527	0.099	0.0964	0.1593	0.1533	0.232	0.2219	0.311	0.296	0.39	0.371	.4555	0.4412	0.515	0.4952	.55	.5272	0.569
N—C_4H_{10}	0.0035	0.0085	0.0082	0.0175	0.0167	0.0321	0.0305	0.054	0.0511	0.0837	0.0792	.119	0.1114	0.156	0.1446	.1926	.1779	0.227
iso—C_5H_{12}																		
N—C_5H_{12}																		
C_7H_{16}																		
Total	0.9975	1.000	1.000	1.000	1.000	0.999	0.999	1.000	1.000	1.000	1.000	.999	1.000	1.000	1.000	.999	.999	1.000

MOL FRACTION IN LIQUID OR VAPOR

	y_{10}	x_{10}	y_{11}	x_{11}	y_{12}	x_{12}	y_{13}	x_{13}	y_{14}	x_{14}	y_{15}	x_{15}	y_{16}	x_{16}	y_{17}	x_{17}	y_{18}	x_{18}
Temp. (°F.)	207		209		211		213		214		215		216		216.5		217	
CH_4	0.00126	0.000057	0.00126	0.000055														
C_2H_6	0.0102	0.0039	0.01	0.0038	0.0099	0.0037	0.00986	0.0037	0.00983	0.00365	0.0098	.00362	.00976	.00361	.00975	0.0036	.00974	0.00359
C_3H_8	0.236	0.1633	0.2028	0.1388	0.1807	0.1224	0.166	0.1118	0.1561	0.1045	0.1495	0.0996	.1452	.0965	.1424	0.0945	.1405	0.093
iso—C_4H_{10}	0.5442	0.574	0.5487	0.568	0.5432	0.556	0.5322	0.541	0.5192	0.525	0.5022	.503	.4847	.483	.4667	0.4635	.4487	0.4445
N—C_4H_{10}	0.2091	0.26	0.239	0.29	0.266	0.318	0.2916	0.344	0.3149	0.369	0.3376	.393	.3596	.416	.3801	0.4385	.4006	0.46
iso—C_5H_{12}																		
N—C_5H_{12}																		
C_7H_{16}																		
Total	1.000	1.001	1.001	1.000	1.001	1.000	1.000	1.000	1.001	1.000	0.999	.999	.999	.999	.999	1.000	.999	1.001

TABLE X. RESULTS OF ALGEBRAIC METHOD

MOL FRACTION IN LIQUID OR VAPOR

	y_{19}	x_{19}	y_{20}	x_{20}	y_{21}	x_{21}	y_{22}	x_{22}	y_{23}	x_{23}	y_{24}	x_{24}	y_{25}	x_{25}	y_{26}	x_{26}	y_{27}	x_{27}
Temp. (°F.)	218		219		219.5		220		220.5		221		222		222.5		223	
CH_4																		
C_2H_6	0.00973	0.00357	0.00971	0.00354	0.00969	0.00353	.00968	0.00352	.00967	.00351	.00966	0.0035	0.00965	0.0035	.00965	0.00348	.00963	0.00346
C_3H_8	0.1392	0.0919	0.1382	0.0905	0.1369	0.0896	.1361	0.089	.1356	.0885	.1351	0.088	0.1347	0.0874	.1341	0.0868	.1336	0.0861
iso—C_4H_{10}	0.4317	0.425	0.4142	0.407	0.3975	0.389	.3812	0.3715	.3652	.354	.3497	0.338	0.3352	0.322	.3207	0.307	.3072	0.292
N—C_4H_{10}	0.4199	0.48	0.4381	0.499	0.4556	0.517	.4716	0.535	.4881	.552	.5036	0.5675	0.5176	0.5815	.5301	0.592	.5396	0.60
iso—C_5H_{12}					0.0002	0.0004	.00036	0.00068	.00061	.0011	.001	0.00193	0.00175	0.00323	.00293	0.00538	.00488	0.00887
N—C_5H_{12}					0.0001	0.0002	.00018	0.00039	.00035	.00076	.00089	0.00147	0.00133	0.00282	.00255	0.00537	.00486	0.01
C_7H_{16}																		
Total	1.000	1.000	1.000	1.000	0.999	0.999	.999	1.000	.999	.999	.999	1.000	1.000	1.000	.999	1.000	.999	1.000

MOL FRACTION IN LIQUID OR VAPOR

	y_{28}	x_{28}	y_{29}	x_{29}	y_{30}	x_{30}	y_{33}	x_{33}	y_{34}	x_{34}	y_{35}	x_{35}	y_{36}	x_{36}	y_{37}	x_{37}	y_{38}	x_{38}	y_{39}	x_{39}
Temp. (°F.)	225		227.5		230		265		266.5		267		268		269		270		270.5	
CH_4																				
C_2H_6	.00961	.00343	.00958	0.0034	0.00956	0.00335														
C_3H_8	.1329	.0852	.1321	0.0839	0.131	0.0819	0.0582	.0317	.042	.0226	.03	.0161	0.0214	.0115	0.0152	.008	.0107	.0057	.0075	0.004
iso—C_4H_{10}	.2932	.276	.2792	0.262	0.2662	0.243	0.199	.1563	.196	.154	.193	.1515	0.19	.1485	0.1856	.144	.1797	.1393	.1735	0.1344
N—C_4H_{10}	.5466	.602	.5486	0.595	0.5426	0.576	0.62	.5588	.0634	.5688	.648	.5785	0.661	.5848	0.669	.5898	.676	.5958	.684	0.6008
iso—C_5H_{12}	.008	.0143	.013	0.0226	0.0205	0.035	0.0597	.078	.061	.0787	.0619	.0793	0.0628	.08	0.0637	.0806	.0646	.0817	.066	0.0825
N—C_5H_{12}	.00914	.0188	.017	0.034	0.0308	0.061	0.0382	.0571	.0392	.0576	.0398	.0581	0.0404	.0585	0.041	.0586	.0412	.0559	.0416	0.0595
C_7H_{16}							0.0249	.1157	.0256	.1158	.0258	.1161	0.0262	.1165	0.0267	.1165	.0267	.1166	.0268	0.1167
Total	.999	.999	.999	1.000	1.000	1.000	1.000	.998	.998	.998	.999	.999	1.001	.999	1.001	.998	.999	.998	0.999	0.998

TABLE X. RESULTS OF ALGEBRAIC METHOD

MOL FRACTION IN LIQUID OR VAPOR

	y_{40}	x_{40}	y_{41}	x_{41}	y_{42}	x_{42}	y_{43}	x_{43}	y_{44}	44	y_{45}	x_{45}	y_{46}	x_{46}
Temp. (°F.)	271		271.5		272		273		274		276		283	
CH_4														
C_2H_6														
C_3H_8	0.0053	0.0028	.00376	0.002	0.0026	0.0014								
iso—C_4H_{10}	0.167	0.1295	.1607	0.1245	0.1538	0.1191	0.1468	0.1129	0.1385	0.1065	0.13	0.10	0.1216	0.0907
N—C_4H_{10}	0.69	0.6058	.697	0.6088	0.701	0.6118	0.705	0.6108	0.704	0.6088	0.70	0.5988	0.6875	0.5731
iso—C_5H_{12}	0.067	0.0837	.0686	0.0853	0.0707	0.0878	0.0741	0.0904	0.0775	0.0945	0.0829	0.1005	0.091	0.1051
N—C_5H_{12}	0.0423	0.0604	.0435	0.0612	0.0446	0.0628	0.0467	0.0649	0.0495	0.0687	0.0545	0.0746	0.0624	0.0821
C_7H_{16}	0.0269	0.1169	.0272	0.117	0.0274	0.1177	0.0283	0.118	0.0287	0.1194	0.0305	0.1261	0.0394	0.149
Total	0.999	0.999	1.000	0.999	1.000	0.999	1.000	0.997	0.998	0.998	0.998	1.000	1.001	1.000

MOL FRACTION IN LIQUID OR VAPOR

	x_{15}	y_{16}	x_{16}	y_{17}	x_{17}	y_{18}	x_{18}	y_{19}	x_{19}	y_{20}	x_{20}	y_{21}	x_{21}	y_{22}	x_{22}
Temp. (°F.)		216		217		219		220		222.5		226		230	
CH_4															
C_2H_6	.00362	.00976	.0036	0.00975	0.0036	0.00974	.00355	.0097	.0035	.00967	.00349	.00964	0.00344	0.0096	.00335
C_3H_8	.0996	.1452	.0965	0.1423	0.0942	0.1403	.092	.1383	.0905	.1369	.0885	.1351	0.0863	0.1332	.0832
iso—C_4H_{10}	.5022	.4837	.481	0.4642	0.459	0.4452	.437	.425	.4125	.4027	.386	.3787	0.359	0.3542	.325
N—C_4H_{10}	.392	.3586	.415	0.3796	0.435	0.3976	.452	.413	.467	.4262	.477	.4356	0.4755	0.4341	.462
iso—C_5H_{12}	.002	.00178	.0034	0.0031	0.006	0.0054	.0103	.00928	.0173	.0157	.0288	.0261	0.0462	0.0418	.0715
N—C_5H_{12}				0.001	0.0022	0.002	.0044	.00396	.0085	.0077	.0162	.0147	0.0301	0.0272	.0533
C_7H_{16}															
Total	.999	.999	.999	1.000	1.000	1.000	.999	.999	.999	.999	.999	.999	1.000	1.000	.998

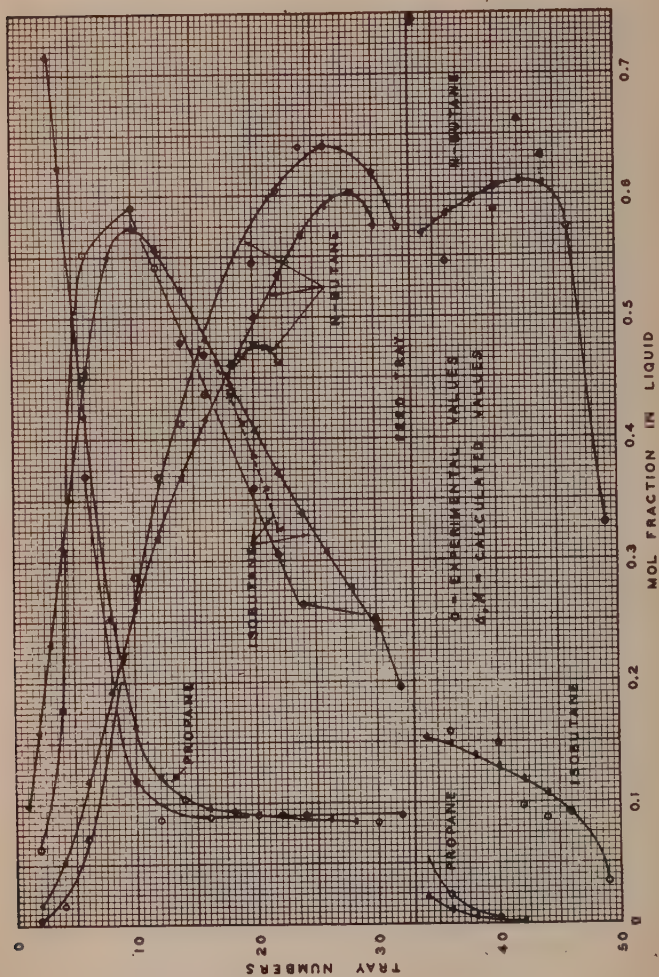
TRAY NUMBERS
MOL FRACTION IN LIQUID
PROPANE
ISOBUTANE
N-BUTANE
FEED TRAY
O - EXPERIMENTAL VALUES
C, M = CALCULATED VALUES

FIG. 13

Composition of Feed Plate

The composition of the liquid on the feed plate was calculated by applying Equation (13) to those components more volatile than isobutane and by applying Equation (14) to those components less volatile than normal butane. The quantity of distillate (D) is the sum of the overhead product and the sidestream, and the composition of the distillate is the composite of these two products. On this basis the compositions of the liquid and vapor at the feed plate were determined to be as follows:

COMPOSITIONS AT FEED PLATE—TEMPERATURE 256° F.

	x_f	K 300 lbs./sq. in. abs. 256° F.	y_f
CH_4	.00015	9.6	.00142
C_2H_6	.00305	3.18	.00979
C_3H_8	.0649	1.78	.1157
iso-C_5H_{12}	.0698	.717	.0501
n-C_5H_{12}	.0529	.63	.03235
C_7H_{16}	.1129	.193	.0218
	0.3037		0.2312

Denoting iso-butane by the subscript d and normal butane by the subscript e

$$x_{d_f} + x_{e_f} = 0.6963$$

$$1.205\ x_{d_f} + 1.06\ x_{e_f} = 0.7688$$

$$x_{d_f} = 0.207$$

$$x_{e_f} = 0.489$$

$$y_{e_f} = 0.519$$

Because of the withdrawal of a side-stream and the effect of vaporization in the reboiler, the column should be divided into four sections; (1) the top six plates above the side-stream, (2) the section between the feed plate and the side-stream, (3) the section between the feed and lowest plate for which analytical data are available, and (4) the remainder including the reboiler.

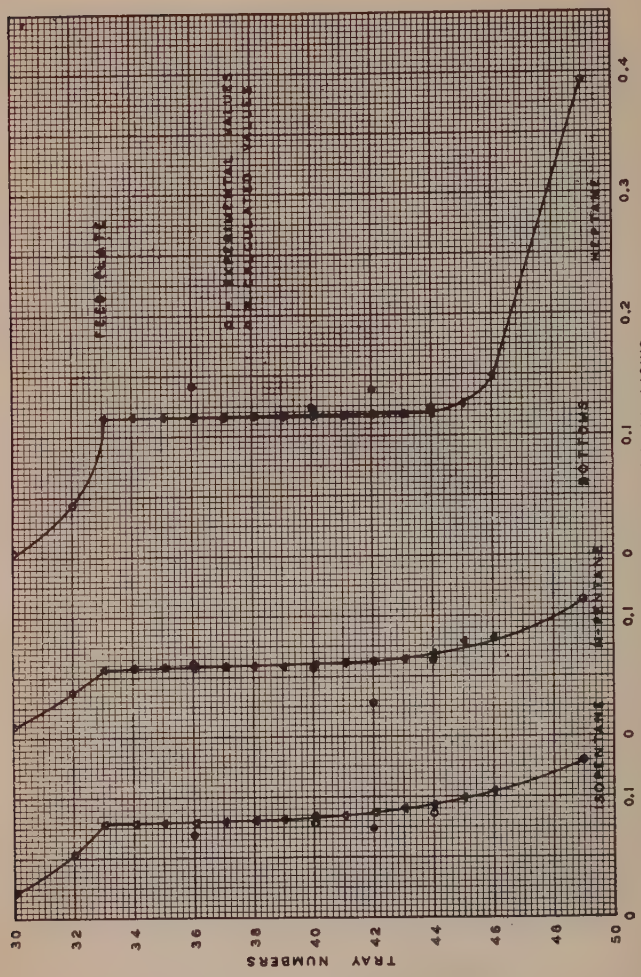
FEED ASSAYS
O.P. EXPERIMENTAL VALUES
P.R. CALCULATION VALUES
ISOPENTANE
N-PENTANE
BOTTOMS
MIDPOINT
MOL FRACTION IN LIQUID
TRAY NUMBERS
0.1
0
0.1
0.2
0.3
0.4
30
32
34
36
38
40
42
44
46
48
50

FIG. 14

Number of Plates Between Plate 7 and Top of Column

This section is operating as an absorber of n-butane. The mol fraction of n-butane in the vapor entering this section is obtained from a material balance around the top of the column and above plate 7;

$$y_{e_7} = 0.905 \times 0.0713 + 0.0956 \times 0.0357 = 0.0649$$

The temperature of plate 6 was observed as 190° F. and the temperature of the top plate 130° F.

Applying the absorption factor method to n-butane above the side stream,

$$K_A = \frac{0.72 + 0.40}{2} = 0.55$$

$$A = \frac{L}{K_A V} = \frac{0.95}{0.55} = 1.727$$

$$\frac{y_7 - y_1}{y_7 - K_1 x_R} = \frac{y_7 - y_1}{y_7 - K_1 y_1} = \frac{0.0649 - 0.0035}{0.0649 - 0.4 \times 0.0035} = 0.967$$

Using this value in Equation (20) (Fig. 7) indicates that 5 equilibrium plates are required above the side-stream. Although there are six plates in this section of the column, two of them were dry during this test as the reflux was introduced on the third plate as indicated in Figure 8, and the number of actual working plates is uncertain. If it is assumed that the two dry plates did no work, the indicated overall plate efficiency is apparently 125%. But if it is assumed that the two dry plates were roughly equivalent to one normal plate, the overall plate efficiency is apparently 100 per cent.

Number of Plates Between Feed Plate and Plate 6

This section is operating as an absorber of n-butane. Assuming a linear temperature distribution the temperature of the plate above the feed plate is calculated as 254°F. The equilibrium temperature of plate 7 is 193°F.

Applying the absorption factor method to n-butane,

$$K_A = \frac{1.05 + 0.73}{2} = 0.89$$

$$A = \frac{L}{K_A V} = \frac{0.905}{0.89} = 1.017$$

$$\frac{y_t - y_7}{y_t - K_7 x_6} = \frac{0.5190 - 0.0649}{0.5190 - 0.0520} = 0.9724$$

Using this value in Equation (20) indicates that 28 equilibrium plates are required. Since there are 26 actual plates in this section, the overall plate efficiency is 108% on the basis of the values of the equilibrium constants used without any correction for deviation from ideal solutions.

Because the feed heater is not an equilibrium apparatus and because the actual feed plate is not an equilibrium plate, the vapor rising to the plate above is actually more volatile than the equilibrium vapor calculated for use with the absorption factor method. This results in actual temperatures much lower than the calculated temperatures for plates immediately above the feed, and a corresponding adjustment of the compositions so that the concentration of n-butane in the actual column passes through a maximum above the feed plate. This maximum is not introduced in calculations by the absorption factor method, and hence the absorption factor may be applied to n-butane in this part of the column if calculated temperatures rather than actual temperatures are used. This procedure should always be followed as in computing the number of equilibrium plates, equilibrium temperatures are of significance, rather than actual temperatures.

Number of Plates Between Feed Plate and Plate 47

This section is operating as a stripper of isobutane. The mol fraction of isobutane in the vapor entering this section ($y_{d_{47}}$) is obtained from a material balance around the bottom product and between plates 46 and 47;

$$y_{d_{47}} = 1.325 \times 0.0907 - 0.325 \times 0.0347 = 0.1089$$

The equilibrium temperature of plate 46 is calculated as 283°F., and the temperature of the plate below the feed plate as 258°F.

Applying the stripping factor method to isobutane,

$$K_s = \frac{1.34 + 1.23}{2} = 1.285$$

$$S = \frac{K_s \bar{V}}{\bar{L}} = \frac{1.285}{1.325} = 0.970$$

$$\frac{x_f - x_{46}}{x_f - \frac{y_{47}}{K_{46}}} = \frac{0.207 - 0.0907}{0.207 - \frac{0.1089}{1.34}} = 0.924$$

Using this value in Equation (20) indicates that 14 theoretical plates are required. With 13 actual plates, the overall plate efficiency is 108% on the basis of the ideal equilibrium constants.

Checking the assumed temperature of the feed plate (256°F.) by the linear temperature equation

$$t_f = 193 + \frac{28}{42}(283 - 193) = 193 + 60 = 253°\ \text{F.}$$

Number of Plates Below Plate 46

This section includes the reboiler and operates as a stripper of isobutane. The calculated equilibrium temperature at the reboiler is 350°F. and at plate 47 is 300°F.

Applying the stripping factor to isobutane,

$$K_s = \frac{1.67 + 1.42}{2} = 1.545$$

$$S = \frac{K\bar{V}}{\bar{L}} = \frac{1.545}{1.325} = 1.166$$

$$\frac{x_{46} - x_m}{x_{46} - \frac{y_{m+1}}{K_m}} = \frac{x_{46} - x_B}{x_{46} - \frac{x_B}{K_B}} = \frac{0.0907 - 0.0347}{0.0907 - \frac{0.0347}{1.67}} = 0.801$$

Using this value in Equation (22) indicates that 3 theoretical plates are required. There are 3 actual plates including the reboiler as one plate.

Correct Location of Feed Plate

Since this column is separating a complex mixture between two adjacent components, isobutane and normal butane, the correct location of the feed plate may be determined from Equations (18) and (18a). According to Equation (18a) the feed plate is correctly located when

$$\frac{x_{d_f}}{x_{e_f}} > .4238$$

The value for this ratio on the feed plate is 0.4239. Similarly the terms of Equation (18) reduce to substantial equality with this feed plate composition. Since the inequalities become equalities for the special case of minimum reflux, we may conclude that the solution obtained by means of the absorption factor method is not only that solution which correctly indicates the operation of the column, but in this case is also the solution which requires the least number of plates for a given separation under the existing operating conditions. Because of the large number of plates included in the column, it is to be expected that the composition on the feed plate would approximate that obtained under conditions of minimum reflux (infinite number of plates).

Conclusions

From the comparison of actual plant test data with the computed results obtained by the application of the absorption factor method to the calculation of this gasoline stabilizer, it seems that the absorption factor method offers a simple and reliable method for computing the number of equilibrium plates required in commercial gasoline stabilizers, and probably other similar equipment in which the equilibrium conditions between liquid and vapor may be assumed to follow the relationships of ideal solutions.

Nomenclature

F = Moles of feed to column; used as subscript to signify feed.
B = Moles of bottom product; used as subscript to signify bottom product.
D = Moles of distillate withdrawn as overhead product; used as subscript to signify overhead product.

V = Moles of vapor rising from plate in rectifying section; used as subscript to signify vapor phase.
L = Moles of liquid overflowing from plate in rectifying section; used as subscript to signify liquid phase.
$\bar{V}$ = Moles of vapor rising from plate in stripping section.
$\bar{L}$ = Moles of liquid overflowing from plate in stripping section.
a, b, c, d, etc., refer to moles of individual components of which a is the most volatile; when used as subscript the letters refer to individual components.
x = Mole fraction of any component in the liquid.
y = Mole fraction of any component in the vapor.
n = Number of theoretical plates above feed plate; used as subscript, refers to any plate in rectifying section.
m = Number of theoretical plates below feed plate; used as subscript, refers to any plate in stripping section.
f = feed plate, i.e., plate from which the vapor rising becomes the feed to the rectifying section and liquid overflowing becomes the feed to the stripping section.
M = Bottom plate of column.
1, 2, 3, etc., refer to the first, second, third, etc., plate of the column, numbering from the top downward.
P = Total pressure.
p = Vapor pressure of pure component.
K = Equilibrium constant for a particular component.
$A = L/KV$ = absorption factor for a particular component.
$S = KV/L$ = stripping factor for a particular component.

Heat Quantities

H = "Total heat" Enthalpy (above convenient datum temperature) of one mole of vapor.
h = "Total heat," Enthalpy of one mole of liquid.
Q_c = Heat quantity removed by condenser in unit time.
Q_r = Heat quantity supplied by kettle in unit time.
U = Change in quantity of flowing liquid caused by the introduction of the feed at temperature of feed plate. This is equivalent to the ratio: difference in enthalpy between vapor feed at temperature of feed plate, and feed as delivered to column, divided by molal heat of vaporization at temperature of feed plate

$$= \frac{F(H_f - H_F) + F_L(H_F - h_F)}{H_f - h_f}$$

T = Absolute temperature °F. + 460.
t = temperature in degrees Fahrenheit.

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PLATE EFFICIENCIES IN RECTIFICATION OF BINARY MIXTURES

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The mechanism of rectification in a bubble cap column involves primarily the interaction of a vapor bubble rising through a liquid. Preliminary analysis leads to the conclusion that, for constant slot width, in a given liquid, the bubble diameter should be relatively independent of rate of flow of the vapor. Consequently, for a given liquid depth, the rate of rise of the bubble and hence its time of contact with the liquid should depend but little on the rate of vapor flow. This leads to the conclusion that, however high the vapor rate, so long as vapor does not escape vigorously below the skirt of the cap or entrainment become excessive, plate efficiency should be influenced but little by vapor rate. Since the rate of interaction of the bubble with the liquid around it should be proportional to the distance yet to go to equilibrium, one would expect the logarithm of 100 minus the per cent efficiency to be substantially linear with the time of contact of the bubble with the liquid, or what is the equivalent to the same thing, to the depth through which the bubble must rise. Furthermore, it is difficult to see how superficial velocity of the vapor can have any marked effect on the plate efficiency except at unduly low or excessively high velocities. Finally, for a component of roughly the same molecular weight and liquid viscosity, analysis indicates that the plate efficiency should be relatively independent of the nature of the constituent or the character of the vapor liquid equilibrium.

While the concept of bubble plate action just outlined has long been held and has served as a basis for our computations of column performance, data to justify it have been lamentably limited. This article presents data quantitatively substantiating these conclusions as applied to the rectification of binary mixtures, as widely different in

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character as benzene-toluene, ethanol-water, and aniline water, in various types of experimental equipment from a ten-plate column to a single-plate column, and with plate efficiencies determined not merely by overall performance of the columns but by plate-to-plate analysis of the liquid.

The first group of variables not covered includes the closeness of packing of the bubble caps and the spacing of the plates. The second includes the effects of superficial velocity and liquid depth, perhaps together with cap design, on entrainment ratios. It is felt that Figures 3 and 4 at least give the designer of rectifying equipment the cue to the character of the influence of the more important variables affecting the efficiency of bubble-cap columns.

In 1927, when this program was begun, there were practically no published data to show whether the standard methods of computing the concentration change from plate to plate in a distillation column were reliable. Accordingly, rectification studies were begun, and results for multicomponent systems have been published by Lewis and Wilde [1] and by Lewis and Smoley.[2]

The purpose of this paper is to present some of the results obtained in the steady state rectification of *binary* mixtures, in experimental bubble-cap columns located in the Chemical Engineering Laboratory of the Massachusetts Institute of Technology. The mechanism of the bubbling of gases through liquids is also considered.

Studies of Bubble-Cap Action

In order to obtain information on the mechanics of flow of vapors through slots of bubble caps immersed in liquids, a few experiments were made on the flow of air through single bubble caps immersed in water. As the gauge pressure of the air inside the caps is increased by steps, the water level inside the cap is depressed, uncovering the slot to various extents, with corresponding changes in the rate of air flow. When the water level inside the cap is depressed but little (one-sixth of an inch in one case), an air bubble clings in the upper part of the slot, probably due to the effect of surface tension. Fig. 1 shows a plot, on logarithmic paper, of slot opening L in inches, vs. rate of air flow, expressed as $q = Q/Nw$, where

Q is the cubic feet per minute,
N is the number of slots per plate, and
w is the slot width in inches.

The plot is based on data of Carey,[3] of Griswold,[4] and of Rogers and Thiele.[5] At the higher values of q, the data can be represented roughly by a straight line having a slope of two-thirds, as required by the recent equation of Rogers and Thiele, derived from the equation for gas flow through orifices.

Fig. 2 shows data of Volante [6] for the pounds of water carried per 100 pounds of air to various heights above the plate, plotted vs. q. The cap used by Volante is the same as those employed in rectifying

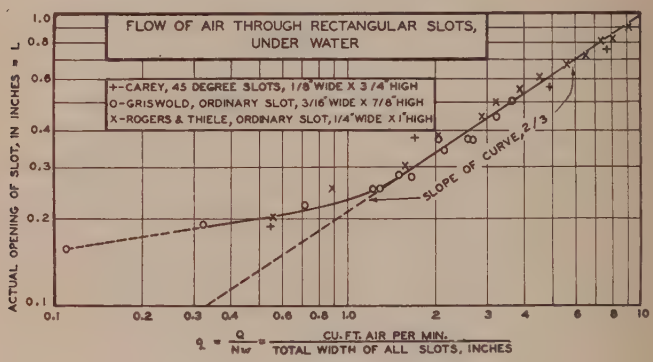

Fig. 1

benzene-toluene mixtures in the 7-plate column, and is described in detail in Table 1. In general, at a given distance above the plate, entrainment ratio increased very rapidly with increase in vapor rate; at a given vapor rate the entrainment ratio decreased with increase in distance above the plate. At the highest air rate employed ($q = 3.44$, $V = 0.738$ f.p.s.), 100 pounds of air carried 6.6 pounds of water at a distance 7 inches above the plate, 1.2 pounds 9 inches above the plate, and 0.13 pounds 15 inches above the plate; the slots were about two-thirds open. The data of Chillas and Weir [7] and of Souders and Brown [8] show the same general effect of vapor velocity upon entrainment.

In a given plate with a given overflow construction, increasing vapor rate tends to increase time of contact, since some of the bubbles escape at a lower level (Fig. 1) and must travel through a greater depth of liquid, and since entrainment tends to increase (Fig. 2). Furthermore, greater vapor velocity usually corresponds to increased

TABLE 1.—DESCRIPTION OF RECTIFYING COLUMNS EMPLOYED

Number of plates in column	10	7	1
Inside diameter of column, inches	8	8	6
Distance between plates, inches	16	12.3	10
Number of caps per plate	1	1	1
Height of cap, inches	2	2	3.25
Outside diameter of circular cap, inches	Note 1	4.13	2.38
N, Number of slots per plate	48	36	32 to 4
w, Width of each slot, inches	3/16	1/8	1/6 to 1/2
Nw, Total width (inches) of all slots per plate	9	4.5	2
Height of vertical rectangular slots, inches	7/8	3/4	1/2
Clearance between bottom of slot to plate, inches	1/8	1/8	0
h, Height of overflow pipes, inches	1.5	1	Note 2
i_o, Height of overflow pipe less height top of slot, in.	1/2	1/8	Note 2
Height of vapor riser, inches	1	1.25	2.63
Inside diameter of vapor riser, inches	Note 1	2.19	1.05
Angle of slot with radii of cap, degrees	0	45	0
Center-to-center, riser and overflow pipes, inches	.....	3.5	2.25
Inside diameter of overflow pipe, inches	1.5	1.05	0.493
(a) Superficial cross-section of column, sq. in.	50.3	50.3	28.3
(b) Nominal area of slots (wide open), sq. in.	7.88	3.37	1.0
100 (b)/(a), per cent	15.6	6.7	3.53
(c) Cross-section of vapor risers, sq. in.	8.0—	3.77	0.864
100 (c)/(a), per cent	15.9—	7.5	3.05
Thickness of insulation on column	1	1 to 2	1
Means of keeping insulation warm	Flue gas	None	Elec.Ht.

NOTE 1. The cap was of rectangular cross-section, 2-in. wide, and extended entirely across the column. The vapor riser was 1-in. wide, 1-in. high, and extended across the column.

NOTE 2. The overflow pipe was adjustable, to give various liquid depths on the plate, and in the ethanol-water runs, the overflow pipes were always lower than the vapor risers. The values of i are given in Fig. 3. In the benzene-toluene runs, the caps were 2.25-in. in dia. and 1.5-in. high; the vapor riser was $\frac{11}{16}$-in. high and the overflow pipe was $\frac{13}{16}$-in. high, other dimensions were the same as in Table 1.

NOTE 3. A gas-fired still[2] was used on the 10-plate column. The still of the 7-plate column was heated by dry steam condensing inside a coil of standard 1-in. steel pipe, 7.84 ft. long (in form of a helix) and having 2.7 sq.ft. of external heating surface. The still of the single-plate column was heated electrically by immersion heaters, and the insulation was electrically heated to prevent refluxing.

reflux, which backs up a deeper liquid level over the overflow weirs. On the other hand, at very high vapor rates, the vapor can "cone" the liquid back from the cap, particularly when blowing under the skirt. Likewise, the inner layer of a thick stream of bubbles rising from the slots contacts only with liquid which is already somewhat denuded of volatile constituents by contact with the outer layer of

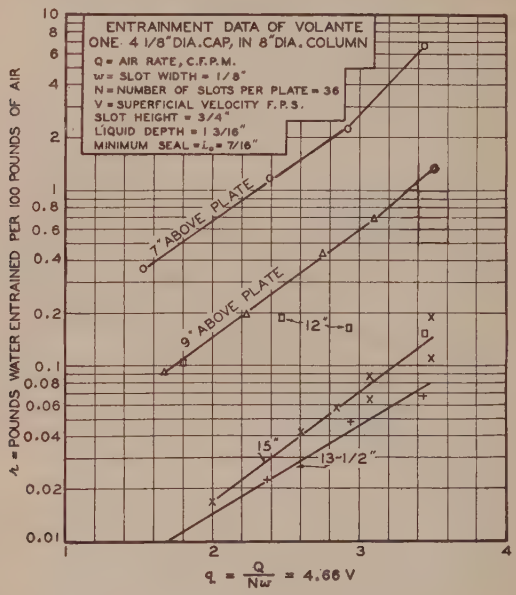

FIG. 2

bubbles. Change of bubble size itself with vapor rate is uncertain, so long as the slots are not overloaded, but probably this change is slight. The net result is a counterbalancing effect of opposing factors, none of which is important in the normal range of operation of the slots. Consequently, one would anticipate substantial constancy of plate efficiency for a given plate over wide ranges of vapor velocity, marked variations developing only at velocities which are either unduly low or excessively high. Overall enrichment is, of course, unfavorably affected by actual entrainment of liquid from one plate to the next, and excessive vapor velocity builds up enough back-

pressure on the plate below to force liquid up through the overflow pipes.

Decrease in slot width gives a larger ratio of bubble surface to bubble volume, and should increase plate efficiency, particularly at the lower vapor rates. Increase in depth of liquid on the plate obviously should tend to increase plate efficiency, but may result in the formation of waves in the pool, accompanied by a spasmodic or intermittent type of bubbling and increased entrainment to the plate above, to the detriment of overall enrichment.

Rectification

Granting that equilibrium and thermal data are available, the design of bubble-plate columns for rectification involves the calculation of (1) the number of plates required to produce the desired enrichment and (2) the cross-section required to handle the desired capacity. The remainder of the paper will deal with the first of these two problems. In order to obtain data for testing methods of predicting concentration gradients in liquid and vapor streams flowing through a plate column, arrangements were made to obtain samples of liquid from individual plate sections of the columns tested. In all the work reported herein the rectification operation was conducted with total reflux. A charge of liquid is introduced into the system, heat is supplied to the still and cooling water is circulated through the condenser, to obtain steady operating conditions. Under these conditions all vapor leaving the top plate is condensed and returned as reflux to the top plate, and hence the composition of the reflux condensate is the same as that of the vapors leaving the top of the column. Similarly, the composition of the liquid overflowing from any plate is identical with the composition of the vapors entering the plate. In other words, the equation of the operating line is

$$y_{n-1} = x_n \qquad (1)$$

where y and x represent the mol fraction of more volatile component in the vapor and liquid, respectively. As pointed out by Murphree,[9] the composition y_n of the actual vapor leaving plate n will be less than the composition y_n^* of the vapor which in an ideal plate would be in equilibrium with the liquid of composition x_n. This leads to the definition of the Murphree plate-to-plate efficiency:

$$E_n = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \qquad (2)$$

By operating with total reflux the determination of x_n gives not only x_n itself, which is needed for determining y_n^* in Equation (2), but also gives y_{n-1}, making it unnecessary to attempt to take vapor samples. Obviously, a sample of liquid can be withdrawn from the plates quickly whereas an attempt to remove vapor would upset the operation since the desired size of vapor sample in many cases would be larger than the vapor space above the plate.

Table I gives the dimensions of the three bubble plate columns employed. The 10-plate column had one "tunnel-cap" per plate and is described fully by Lewis and Smoley.[2] The single-plate and 7-plate columns had one circular bubble-cap on each plate. When steady operating conditions had been obtained, samples of the liquids were quickly drawn from the various plates and analyzed† by determining the boiling point of the sample in a Cottrell true-boiling-point apparatus, and reading the barometer. Mixtures of ethanol and water were rectified in a single-plate column, and the equilibrium relation between vapor and liquid compositions was measured experimentally.[10] The binary mixture used in the multiple-plate columns was benzene-toluene. Rosanoff, Bacon and Schulze [11] had shown that the total vapor pressures exerted by mixtures of benzene-toluene at one temperature (79.9° C.) corresponded closely to those calculated by Raoult's and Dalton's Laws. As a check, Cottrell boiling points were determined for a number of known mixtures of benzene and toluene boiling at atmospheric pressure and these agreed closely with those calculated from Raoult's and Dalton's Laws, employing the vapor pressure data of Young for benzene and of Kahlbaum for toluene. The mol fractions of benzene in the sample drawn from the column were calculated from the Cottrell boiling points as outlined above, and given in Tables 2 and 3. In the case of the 10-plate column, the composition of the liquid in the still is not shown because of the possibility of vapor having contaminated the samples. The individual plate-to-plate efficiencies, E_n, were calculated by means of Equations (1) and (2) from the data in Tables 2 and 3, and are tabulated. The efficiency of the top plate is not reported, since with

† This procedure was used in the benzene-toluene runs. The ethanol-water mixtures were analyzed by specific gravity measurements, and the aniline-water solutions were analyzed by potentiometric titration with bromine.

TABLE 2.—RECTIFICATION OF BENZENE-TOLUENE MIXTURES WITH TOTAL REFLUX, IN TEN-PLATE COLUMN.
(Data of Griswold.)

Run	G-1		G-2		G-3		G-4		G-5		G-6		G-7	
	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n
Plate 1	0.290	0.63	0.232	0.62	.179	0.72	.084	0.59	.097	0.51	0.094	0.71	0.057	0.65
2	0.420	0.57	0.349	0.64	.297	0.64	.140	0.64	.151	0.52	0.168	0.67	0.102	0.60
3	0.546	0.63	0.487	0.55	.429	0.72	.229	0.69	.228	0.73	0.273	0.69	0.169	0.70
4	0.675	0.56	0.607	0.66	.587	0.65	.355	0.69	.364	0.67	0.412	0.78	0.280	0.72
5	0.768	0.64	0.731	0.61	.713	0.68	.504	0.69	.510	0.69	0.583	0.55	0.427	0.66
6	0.850	0.58	0.818	0.68	.815	0.68	.651	0.70	.657	0.67	0.692	0.71	0.573	0.74
7	0.900	0.58	0.888	0.66	.886	0.69	.772	0.70	.777	0.67	0.804	0.67	0.720	0.69
8	0.935	0.72	0.931	0.78	.933	0.85	.859	0.72	.854	0.69	0.878	0.72	0.822	0.69
9	0.963	0.83	0.964	0.74	.968	0.95	.918	0.68	.913	0.66	0.930	0.83	0.892	0.66
10	0.982		0.981		.987		.952		.947		0.965		0.935	
Reflux	0.995		0.996		1.00—		.983		.973		0.985		0.970	
Ave. E_n		0.64		0.66		0.73		0.68		0.65		0.70		0.68
(1)	17.4		22.6		28.5		29.9		35.2		38.3		54	
(2)	.....		.....		.....		0.7		.....		.....		.....	
(3)	0.32		0.79		1.32		1.28		1.74		1.98		2.38	
(4)	27		30		34.5		22		39.5		35.5		48	
(5)	0.178		0.43		0.715		0.735		0.985		1.07		1.21	
(6)	0.418		1.00		1.67		1.71		2.29		2.49		2.82	

(1) Pressure in Still, Cm. H_2O.
(2) Pressure between Column and Condenser, Cm. H_2O.
(3) Liters of Reflux, per minute.
(4) Reflux Temp., Deg. C.
(5) V = Sup. Vel. of Vapor, F.P.S., at normal barometer and 99° C.
(6) q = 2.33 V = C.F.P.M. per slot, divided by slot width in inches.

TABLE 2.—RECTIFICATION OF BENZENE-TOLUENE MIXTURES WITH TOTAL REFLUX, IN TEN-PLATE COLUMN.
(Data of Griswold.)

Run	G-8		G-9		G-10		G-11		G-12		G-13		G-14	
	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n	x_n	E_n
Plate 1	0.012	0.67	0.075	0.71	0.031	0.58	0.030	0.74	0.042	0.61	0.038	0.66	0.016	0.30
2	0.022	0.50	0.133	0.62	0.054	0.74	0.058	0.50	0.074	0.59	0.069	0.48	0.022	0.59
3	0.036	0.89	0.216	0.66	0.102	0.65	0.093	0.63	0.124	0.50	0.107	0.62	0.039	0.49
4	0.076	0.60	0.337	0.73	0.174	0.61	0.158	0.73	0.188	0.62	0.178	0.59	0.063	0.59
5	0.129	0.65	0.487	0.72	0.272	0.74	0.269	0.68	0.293	0.72	0.274	0.68	0.107	0.62
6	0.214	0.77	0.643	0.73	0.420	0.73	0.405	0.76	0.438	0.71	0.410	0.70	0.178	0.65
7	0.354	0.73	0.772	0.70	0.580	0.72	0.571	0.73	0.594	0.70	0.565	0.65	0.284	0.67
8	0.512	0.69	0.860	0.74	0.721	0.70	0.716	0.70	0.729	0.73	0.696	0.77	0.421	0.68
9	0.659	0.74	0.920	0.81	0.823	0.68	0.821	0.68	0.834	0.74	0.817	0.69	0.571	0.72
10	0.786		0.959		0.892		0.890		0.905		0.888		0.715	
Reflux	0.873		0.979		0.946		0.935		0.960		0.951		0.824	
Ave. E_n		0.70		0.71	..	0.68		0.68		0.66		0.65		0.59
(1)	46.5		63		98		78		91.2		126.6		103.4	
(2)	.....		.....		.....		.....		.....		.....		21.7	
(3)	2.18		2.87		3.32		3.41		3.79		4.37		4.20	
(4)	37		40		49.5		42		38.5		48.4		34	
(5)	1.25		1.52		1.70		1.82		2.07		2.28		2.49	
(6)	2.91		3.54		3.96		4.24		4.83		5.31		5.80	

(1) Pressure in Still, Cm. H_2O.
(2) Pressure between Column and Condenser, Cm. H_2O.
(3) Liters of Reflux, per minute.
(4) Reflux Temp., Deg. C.
(5) V = Sup. Vel. of Vapor, F.P.S., at normal barometer and 99° C.
(6) q = 2.33 V = C.F.P.M. per slot, divided by slot width in inches.

TABLE 3.—RECTIFICATION OF BENZENE-TOLUENE MIXTURES WITH TOTAL REFLUX, IN SEVEN-PLATE COLUMN.

(Data of Page and Wicker.)

Run	PW1 x	PW2 x	PW3 x	PW4 x	PW7 x	PW9** x
Still	0.109	0.046	0.073	0.278	0.089	0.134
Plate 1	0.141	0.095	0.139	0.360		
2	0.263	0.143	0.205	0.538	0.250	0.276
3	0.376	0.225	0.322	0.615	0.363	0.446
4	0.476	0.314	0.486	0.731	0.500	0.543
5	0.600	0.459	0.617	0.813	0.614	0.653
6	0.698	0.564	0.737	0.866	0.746	0.714
7	0.784	0.695	0.853	0.912	0.851	0.771
Reflux		0.789	0.907	0.940	0.911	0.801
Ave. E_n*	0.59	0.65	0.68	0.63	0.65	0.54
(1)	22000	44900	60000	18200	58600	38100
(2)						
(3)	27.1	40.0	49.8	27.0	48.6	
(4)	299	415	444	250	446	350
(5)	0.62	1.27	1.70	0.51	1.66	1.2
(6)	2.89	5.91	7.92	2.38	7.73	5.59

(1) Q/θ in Still, B.t.u./hr.
(2) Reflux Temp., deg. C.
(3) Δt, deg. F. Sat. Temp. of Steam, minus Temp. of Liquid in Still.
(4) U = Overall heat transfer coefficient in still, B.t.u./(hr.) (sq.ft.) (deg. F. diff.).
(5) V = Sup. Vel. of Vapor, F.P.S., at normal barometer and 99° C., calculated from Q/θ, taking the latent heat of an equi-molal mixture as 13,700 B.t.u. per lb. mol.
(6) q = 4.66 V = C.F.P.M. per slot, divided by slot width in inches.

* Average of plate-to-plate Murphree efficiencies of Plates 1–6, inclusive, for Runs 1–4.
** The mixture used in this run was carbon tetrachloride-toluene.

the multiple-plate columns the overhead reflux was substantially colder than the liquid on the top plate which would bring about partial condensation, thus obscuring the rectifying action. The arithmetic average of the plate-to-plate efficiencies is calculated for each run. It is felt that the precision of the data do not warrant the complication of allowing for inequalities in molal latent heats in computing plate efficiencies.

Discussion of Results of Rectification Studies

Effect of Slot Width and Depth of Liquid.—Thirty-two runs were made with ethanol-water in the single-plate column, using a variety

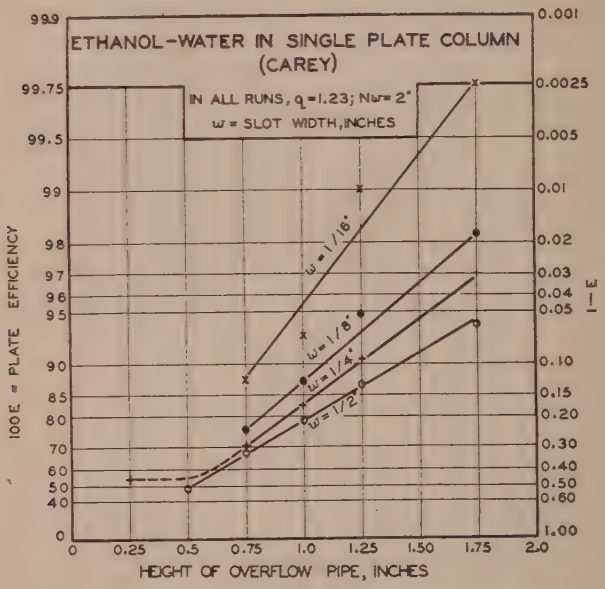

FIG. 3

of single caps, all having slots one-half inch high, and a total slot area of one square inch and a total slot width of two inches. In all these runs the vapor rate was 2.46 cubic feet per minute, or $q = 2.46/2 = 1.23$ C.F.P.M. per inch of total width. The ethanol concentration on the plate was held in the narrow range from 27.5 to 34.2 mol per cent. The vapors from the plate were condensed in a backward-return condenser, and returned as hot reflux to the plate.

It is seen (Fig. 3) that plate efficiency is increased by decreasing slot widths and by increasing the height of the overflow pipes, i.e., by increasing the apparent depth of liquid on the plate.

As suggested by the derivation [9] of the Murphree efficiency, a straight line should result upon plotting the term "—log (1—E)" vs. the time of contact. For runs at a given value of q, the slot opening and liquid head on the overflow pipes are constant, and under such conditions time of contact is linear in apparent liquid depth, and hence the term —log (1—E) should be linear in apparent liquid depth. The averaged data for the runs with ethanol-water, when plotted in this way, (Fig. 3) give substantially straight lines. Above 95% efficiency, very small errors in E appear as large percentage errors in (1—E).

Benzene-toluene runs made in the single plate column, with $q = 1.78$, showed a slight effect of liquid composition on plate efficiency:

TABLE IA

x_n	0.16	0.24	0.36	0.47	0.59	0.68	0.76
E_n	55	53	56	56	58	59	60

Aniline-Water Run.—In a previous investigation [2] on the plate efficiency of individual components in a multi-component mixture in the 10-plate column, there were indications that deviation from Raoult's Law affected plate efficiency, although this appeared unreasonable. A run was made with an aqueous solution of aniline, where the actual volatility of aniline ($y^*/x = 4.8$) is many fold that predicted by Raoult's Law. The following results were obtained, with a superficial vapor velocity of 2.77 f.p.s.

TABLE IB (Griswold)

Plate Number	Mol Per Cent of Aniline	
	Observed	Computed, $E_n = 0.58$
5	0.000473	0.00044
6	0.00136	0.00141
7	0.00463	0.00451
8	0.0130	0.0144
9	0.0459	0.0461
10	0.149	0.1478
Reflux	0.473	0.473

Effect of Vapor Rate.—Additional runs were made [3] on ethanol-water in the single plate column, using various vapor rates and liquid seals, and the results are shown in the upper part of Fig. 4. In the lower part of Fig. 4 values of the average plate efficiency for the benzene-toluene runs are plotted against q, the vapor rate per slot divided by the width of the slot. For any one rectifying column the abscissae are strictly proportional to the superficial velocities of

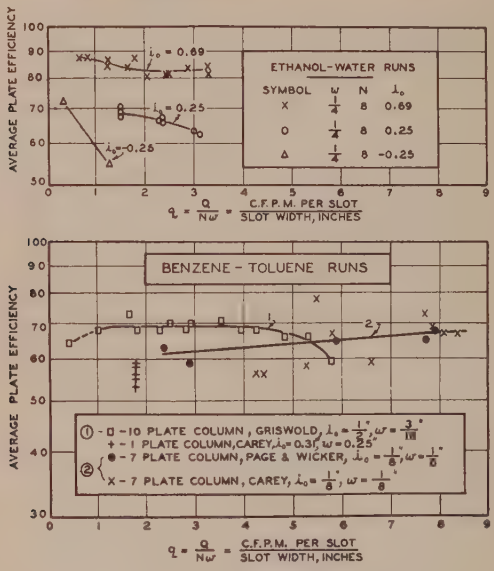
AVERAGE PLATE EFFICIENCY
ETHANOL-WATER RUNS
SYMBOL w N l_o
X 1/4 8 0.69
O 1/4 8 0.25
Δ 1/4 8 -0.25
l_o = 0.69
l_o = 0.25
l_o = -0.25
q = Q/Nw = C.F.P.M. PER SLOT / SLOT WIDTH, INCHES
BENZENE - TOLUENE RUNS
① - □ - 10 PLATE COLUMN, GRISWOLD, l_o = 1/2", w = 3/16"
+ - 1 PLATE COLUMN, CAREY, l_o = 0.31", w = 0.25"
② - ● - 7 PLATE COLUMN, PAGE & WICKER, l_o = 1/8", w = 1/8"
X - 7 PLATE COLUMN, CAREY, l_o = 1/8", w = 1/8"
q = Q/Nw = C.F.P.M. PER SLOT / SLOT WIDTH, INCHES

FIG. 4

vapor, V, defined as cubic feet per second per square foot of gross cross-section of the column.* Further as shown in Fig. 1, actual slot opening, and hence true average velocity through the slots, depends upon q. Referring to the data for the 10-plate column in Fig. 4, it is noted that the average plate efficiency is nearly independent of changes in vapor rate over a fourteen-fold range in velocity. As vapor rate is increased there seems to be a slight increase in efficiency at the lower rates and a slight decrease at the higher rates. However, the change is certainly small; if the efficiency of Plate 1 in Run G-14

* For the 10-plate column V equals q/2.33; for the 7-plate column V equals q/4.66.

were excluded from the average for that run, the indicated decrease in efficiency at high velocity would appear even less.

The data for the 7-plate column are also shown in Fig. 4. The most striking features of the results of both columns are: (1) the small change in efficiency with large change in vapor rate and (2) the fact that the efficiencies of the two columns are so nearly the same, even though the ratio of slot area to column cross-section is 15.6 per cent. for the 10-plate column and 6.7 per cent. for the 7-plate column. It should be noted that the "minimum seal" (vertical distance from the rim of the overflow pipe to the top of the slots) is 1/2" for the 10-plate column and 1/8" in the 7-plate column, and that the slot widths were 3/16" and 1/8", respectively.

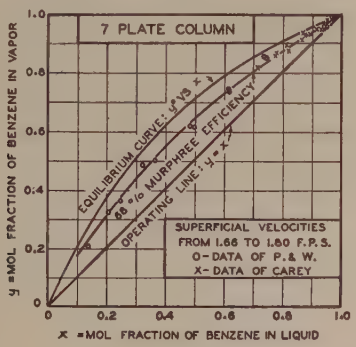

FIG. 5

According to Souders and Brown,[8] from the standpoint of color of distillate, the allowable vapor velocity in the 10- and 7-plate columns would be 1290 and 822 pounds of vapor per hour per square foot of superficial cross-section, while the highest velocities here employed were 1560 and 1130, respectively. The capacity of the 10-plate column was limited by the gas-burning capacity of the furnace heating the still, and not by excessive pressure drop, see Table 2. For $V = 2.5$ f.p.s. ($q = 5.82$), the entrainment from plate to plate was found by a colorimetric method to be 1 mol of liquid per 100 mols of vapor. The capacity of the 7-plate column was limited by the capacity of the overflow pipes.

Lewis and Wilde [1] reported a test on the rectification of naphtha at atmospheric pressure in a column 9 feet in diameter, containing 10

plates, two feet apart. Each plate contained 115 caps, and the total slot area per plate was 10 per cent. of the superficial cross-section of the column. The slots were 1/4 inch in width and 1 inch high, and i_o, the minimum seal, was 1 inch. At $q = 11.7$, $V = 2.8$ f.p.s., average plate efficiency was given as 65 per cent.

Individual Plate Efficiencies.—The actual data for some of the runs in the 7-plate column, which are less consistent than those in the 10-plate column, are plotted on the McCabe and Thiele diagram[12] in Fig. 5. From the definition of the Murphree efficiency, the data should lie in between the equilibrium curve and the operating line in such a way that, for a given x, the height of a given point above

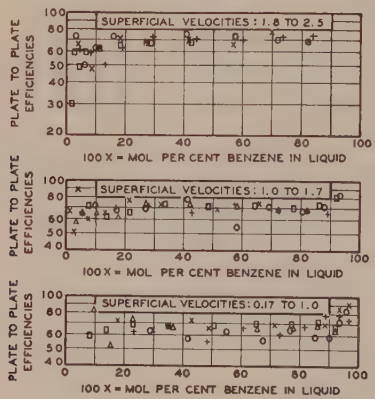
SUPERFICIAL VELOCITIES: 1.8 TO 2.5
SUPERFICIAL VELOCITIES: 1.0 TO 1.7
SUPERFICIAL VELOCITIES: 0.17 TO 1.0
PLATE TO PLATE EFFICIENCIES
100 X = MOL PER CENT BENZENE IN LIQUID

FIG. 6

the operating line, divided by the height of the equilibrium curve above the operating line, equals the efficiency of the individual plate. From Fig. 5 it is seen that, on the whole, the data fall back and forth across the curve for 68 per cent. plate efficiency. These data lend confidence in the usual methods of computing the number of plates required.[12, 13]

An even more drastic test is to plot individual plate efficiencies vs. the actual compositions of liquids on the various plates. In Fig. 6, the 14 runs in the 10-plate column are examined in this way, and since there are nine individual plate efficiencies in each run, Fig. 6 shows 126 points, divided into three groups, according to vapor velocities. In any one of the three parts of the plot, the plate-

to-plate efficiencies for any one run can be identified by a common symbol used in plotting. Fig. 6 gives an indication of increases in individual plate efficiencies, with increase in liquid strength, in the range 0 to 20 and 90 to 100 mol per cent. benzene. When the liquid is very rich or very lean in benzene, both the numerator and denominator of the plate efficiency definition become small, and the resulting precision is poor. Furthermore, an error of one-tenth of one degree Centigrade in determining the Cottrell boiling point of a sample can cause a noticeable deviation in x, and in plate efficiency. In view of these limitations, it is felt that the individual plate-to-plate efficiencies are quite consistent and furnish a remarkable confirmation of the use of the McCabe and Thiele diagram (or the algebraic equivalent) together with the Murphree efficiency.

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A STUDY OF ENTRAINMENT IN A BUBBLE CAP DISTILLATION COLUMN*

By GEORGE E. HOLBROOK † and EDWIN M. BAKER ‡

Published data on actual experimental determinations of the amount of entrainment in bubble cap columns are meager. Chillas and Weir[1] experimentally determined the amount of entrainment in a column with a 16-inch plate spacing when water overflowed the lower plate and air was used as the rising vapor. They actually collected the water carried into the upper plate which would otherwise have been dry and expressed the amount of entrainment as per cent. liquid carried up of the amount overflowing as reflux.

Parrish[2] used three bubble plates and also used the air-water system. He too measured directly the volume of water carried up and expressed it as a percentage of that overflowing.

W. A. Peters[3] recommends a superficial allowable vapor velocity, without "excessive" entrainment, of 1 to 1.3 ft./sec., but does not report experimental data.

A. J. V. Underwood[4] gives a method for relating entrainment to plate efficiency, but records no quantitative data on entrainment.

Souders and Brown[5] present a method of estimating the allowable vapor velocity for operation with a "tolerable" amount of entrainment. They report a few quantitative data on entrainment in a column distilling straw oil, but their method is based on vapor velocities "comparable with satisfactory products." Their empirical method should prove useful in the petroleum field, but care should be exercised in extending it to other systems and conditions where the definition of "satisfactory products" might be quite different from the interpretation imposed in the petroleum field. Furthermore, some work done by the authors indicates that the foaming power of the liquid may, under certain conditions, be more important than the surface tension

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and therefore caution is recommended in the extrapolation of data from one liquid-vapor system to another.

The work of the authors was directed toward the determination of quantitative experimental data on entrainment in a bubble cap distillation column. The variables studied were column vapor velocity, amount of reflux, plate spacing, slot vapor velocity and surface tension. The investigation was confined to the steam-water system. The amount of entrainment was determined by continually introducing a salt solution on one plate and calculating the amount of liquid which must have been mechanically carried to the plate above as entrained liquid in order to raise the salt concentration of the plate above to that found by analysis.

Description of Column and Method of Operation

The column used in this investigation is shown in Fig. 1 and details are shown in Fig. 2. It was an 8-inch diameter bubble cap column with movable plates and a glass observation section. There were two bubble caps on each plate and the plates were fitted with telescoping downpipes to permit their moving up and down in the column while it was in operation. As can be seen in Fig. 1, the middle plate was fixed, but the upper and lower plates could be moved relative to the middle plate. Each movable plate was packed with respect to the containing walls of the column by means of a tubular rubber ring similar to a tire inner tube which could be inflated at will with air. These tubes were held in definite position relative to the plates by means of packing rings held below the plates. The upper movable plate operated in a Pyrex glass cylinder so that that part of the column could be observed while in operation. This section was inclosed by a shatter proof glass casing and hot air was circulated in this jacket to minimize heat losses. The rest of the column and all pipe lines were carefully insulated. A perforated plate was located just a little above the point where the steam was introduced in order to get a uniform cross-sectional vapor distribution below the bottom plate. The rest of the equipment used was essentially the same as that used in standard experimental distillation studies.

Salt brine was heated to approximately the operating temperature of the column and fed continually to the middle plate at the point where the downpipe from the plate above discharged. Sampling lines were placed at the overflow pipe on each plate so that liquid

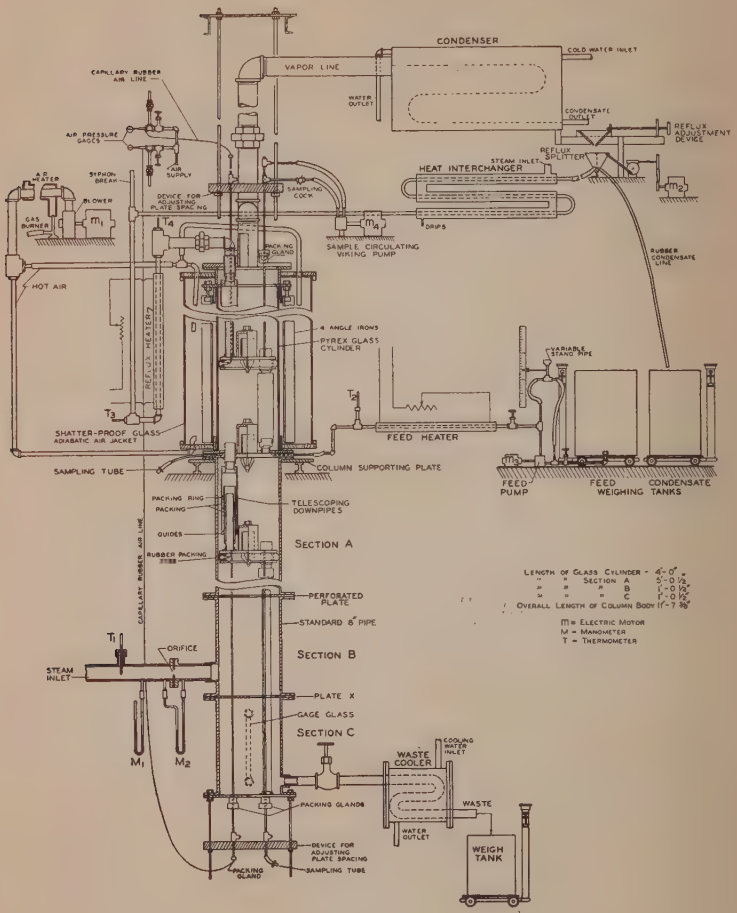
CONDENSER
COLD WATER INLET
VAPOR LINE
WATER OUTLET
CONDENSATE OUTLET
REFLUX ADJUSTMENT DEVICE
CAPILLARY RUBBER AIR LINE
AIR PRESSURE GAGES
AIR SUPPLY
STEAM INLET
REFLUX SPLITTER
HEAT INTERCHANGER
SIPHON BREAK
A.C. WATER
BLOWER
GAS BURNER
DEVICE FOR ADJUSTING PLATE SPACING
SAMPLING COCK
DRIPS
SAMPLE CIRCULATING VIKING PUMP
PACKING GLAND
RUBBER CONDENSATE LINE
HOT AIR
REFLUX HEATER
4 ANGLE IRONS
PYREX GLASS CYLINDER
VARIABLE STAND PIPE
SHATTER-PROOF GLASS ADIABATIC AIR JACKET
FEED HEATER
SAMPLING TUBE
COLUMN SUPPORTING PLATE
FEED PUMP
FEED WEIGHING TANKS
CONDENSATE TANKS
PACKING RING
PACKING
TELESCOPING DOWNPIPES
GUIDES
SECTION A
RUBBER PACKING
CAPILLARY RUBBER AIR LINE
PERFORATED PLATE
STANDARD 8" PIPE
SECTION B
ORIFICE
STEAM INLET
PLATE X
GAGE GLASS
SECTION C
COOLING WATER INLET
WASTE COOLER
PACKING GLANDS
WASTE
WATER OUTLET
WEIGH TANK
DEVICE FOR ADJUSTING PLATE SPACING
PACKING GLAND
SAMPLING TUBE
LENGTH OF GLASS CYLINDER - 4'-0"
" " SECTION A 5'-0 1/2"
" " " B 1'-0 1/2"
" " " C 1'-0 1/2"
OVERALL LENGTH OF COLUMN BODY 11'-7 3/8"
M = ELECTRIC MOTOR
M = MANOMETER
T = THERMOMETER

FIG. 1

BUBBLE CAP
SPIDER
FIXED PLATE
BOTTOM PLATE
TOP PLATE
PACKING RING
PACKING RING
DETAIL OF COPPER BAND
DETAIL OF COPPER BAND
CAP ASSEMBLY
DETAIL OF MOVABLE PLATE
CHIMNEY A'
CHIMNEY B'

FIG. 2

samples could be simultaneously removed from each plate. The vapors rising from the top plate were totally condensed and then split into two fractions one of which discharged into a weigh tank and the other returned to the column as reflux after being heated to the operating temperature of the column in a heat interchanger. A type of reflux splitter which proved very satisfactory is indicated also in Fig. 1. The condensed vapors were discharged into a split trough which discharged into a second trough which oscillated back and forth, thereby splitting the liquid into two portions which were withdrawn from either side of the trough. This device gave a uniformly constant division. The proportions could be varied by moving the point of discharge into the lower trough.

Calculation of the Amount of Entrainment

The actual amount of entrainment under given conditions was determined by heat and material balances. The equation used in the calculations is derived using the following nomenclature.*

S—pounds of steam per hour entering column.
F—pounds of brine per hour entering column.
W—pounds of waste per hour taken from bottom of column.
C—pounds of condensate per hour taken from the condenser and not returned to the column.
O—pounds of overflow per hour from a given plate.
V—pounds of dry steam per hour rising from a given plate.
E—the entrainment expressed as pounds of liquid carried up from one plate to another per pound of dry vapor rising from the lower of the two plates under consideration, i.e., E_2 corresponds to the entrainment from plate 2 to plate 1 as carried up by the dry vapors from plate 2.
R—pounds of reflux per hour entering the top of the column.
X—the concentration of sodium chloride in the liquid expressed as pounds of sodium chloride per pound of solution.
c, 1, 2, 3, etc. as subscripts denote location. Thus the subscripts correspond to the origin of the liquid as
x_c—pounds of sodium chloride per pound of solution in the condensate.
x_1—pounds of sodium chloride per pound of solution on plate 1.
x_2—pounds of sodium chloride per pound of solution on plate 2.

* Weights and compositions could equally as well be expressed in units of mols.

x_3—pounds of sodium chloride per pound of solution on plate 3.

A—pounds of steam condensed per hour in heating the feed up to the temperature of plate 2.

B—pounds of steam condensed per hour in heating the reflux up to the temperature of plate 1.

From the flow sheet of Fig. 3 it is evident that

$$S + F = W + C \quad \ldots\ldots (1)$$

Knowing any three of these variables, one can calculate the fourth. In the actual operation it was most convenient to measure W, F and C and compute S from the above equation. The values so obtained were checked by readings from a calibrated orifice on the steam line.

Since the heat losses from the column were minimized until they were negligible there was essentially no steam condensed due to heat losses up to plate 2 and therefore

$$S = V_3 \text{ and } W = O_3 = O_2 \quad \ldots\ldots (2)$$

Some steam was condensed in the actual operation of the column to heat the feed to the operating temperature of plate 2. Knowing the amount of feed entering per hour and its temperature as it entered the column, and the temperature on plate 2, the amount of heat necessary to bring it up to the temperature of the column could be calculated. Dividing that amount of heat by the latent heat of steam, the pounds of steam condensed per hour to heat the feed could readily be calculated and are designated as A. A similar calculation applied to the reflux gave the pounds of steam condensed on plate 1 per hour in order to heat the reflux to the temperature of plate 1. That amount is designated as B. Since both the feed and reflux were heated to within a few degrees of the operating temperature of the column by heat interchanges, it is evident that A and B were small compared to the amount of vaporization and overflow. It therefore follows that

$$S = V_3 = V_2 + A = V_1 + A + B \quad \ldots\ldots (3)$$

The overall material balance as indicated by balance 1 on the diagrammatic sketch of Fig. 3 leads to

$$V_1 + V_1E_1 = R + C \quad \ldots\ldots (4)$$

and the corresponding salt balance gives

$$V_1E_1X_1 = (R + C)X_c \quad \ldots\ldots (5)$$

Subsituting for (R + C), the above value, we have

$$V_1E_1X_1 = (V_1 + V_1E_1)X_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Solving for E_1, we have

$$E_1 = \frac{V_1X_c}{V_1X_1 - V_1X_c} = \frac{X_c}{X_1 - X_c} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

E_1 represents the amount of liquid per pound of dry vapor carried into the condenser from plate 1 and was always very small compared to E_2.

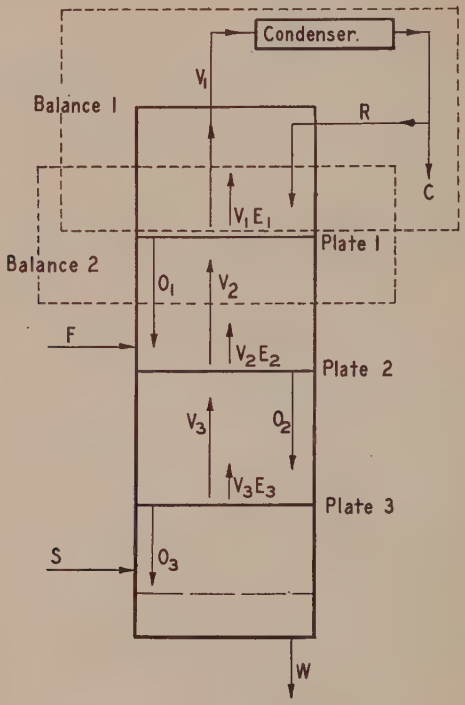

FIG. 3

A total material balance around plate 1 as indicated by balance 2 leads to

$$V_2 + V_2E_2 + R = V_1 + V_1E_1 + O_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

A salt balance around plate 1 leads to

$$V_2E_2X_2 + RX_c = V_1E_1X_1 + O_1X_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Solving for O_1 in Equation (8) and substituting it in Equation (9) gives

$$V_2E_2X_2 + RX_c = V_1E_1X_1 + X_1(V_2 - V_1 - V_1E_1 + V_2E_2 + R) \quad (10)$$

Collecting terms and simplifying

$$V_2E_2(X_2 - X_1) = R(X_1 - X_c) + X_1(V_2 - V_1) \quad (11)$$

Solving for E_2 we have

$$E_2 = \frac{R(X_1 - X_c) + X_1(V_2 - V_1)}{V_2(X_2 - X_1)} \quad (12)$$

This equation can be simplified a great deal by making a very slight approximation. Since V_1 differs from V_2 by the amount of steam condensed to heat the reflux and since that amount of steam condensed was usually less than 2 pounds per hour, the term $X_1(V_2 - V_1)$ could be neglected in comparison to $R(X_1 - X_c)$. This under most conditions did not introduce an error greater than one per cent. E_2 was therefore calculated according to the following equation:

$$E_2 = \frac{R(X_1 - X_c)}{V_2(X_2 - X_1)} \text{ approximately } \pm 1\% \quad (13)$$

Experimental Results

The experimental data obtained from this investigation are given in Table I. Important factors which were varied during the investigation such as plate spacing, bubble cap slot width and total slot area per plate are given in Table I. Furthermore the total pressure drop through the middle plate and the dynamic liquid level above the top of the slots are given also. The dynamic liquid level gives the "effective" head of liquid above the top of the slots while the column is in operation and is not to be confused with the static head of liquid which would correspond to the head of water from the top of the slots to the top edge of the overflow pipe. The pounds of steam per hour rising through the middle plate and the overflow from the top and middle plates per hour were also given as well as the specific volume of the vapor rising through the middle plate. It should be noted that the overflow from the middle plate is greater than that from the top plate by the amount of salt solution fed to the middle plate. Several values for entrainment expressed as pounds of liquid carried up per pound of dry vapor, are given for each run and represent

duplicate calculations based on an equivalent number of liquid samples taken from the various plates. The vapor velocity for each run is expressed as linear and mass velocity for both the column and the

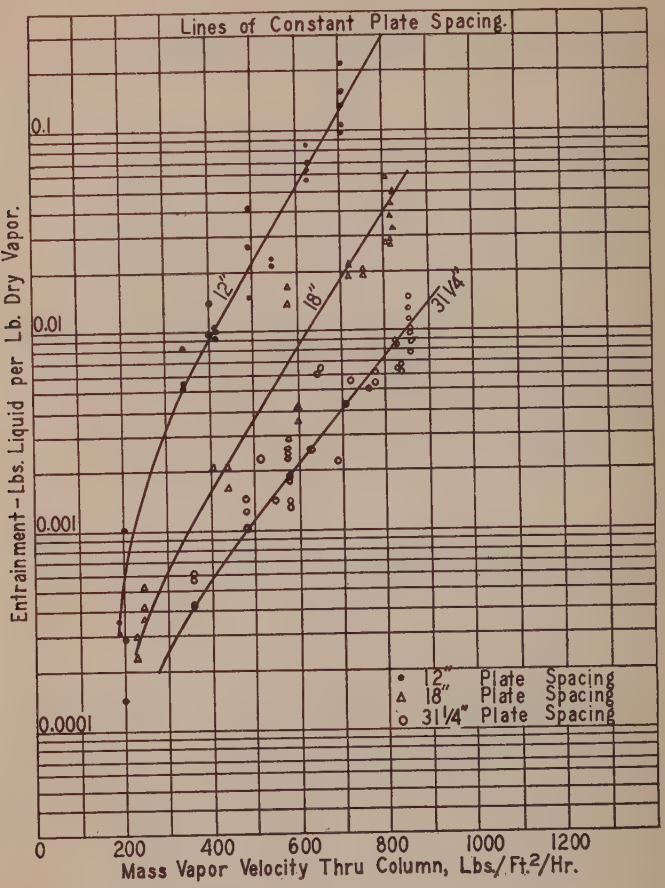

FIG. 4

bubble cap slots. In the former case the velocity is based on the mean free area of the column between the plates and in the latter case it is based on the total area of the bubble cap slots per plate.

TABLE I.

Dynamic Liquid Level Above Top of Slots	Total Pressure Drop through Plate	Pounds per Hour			Specific Volume of Vapor	Entrainment	Vapor Velocity			
		Vapor into Middle Plate	Overflow from Top Plate	Overflow from Middle Plate			Though Column	L	Slot	
In. H_2O	In. H_2O	V_2	O_1	O_2	$Ft.^3/Lb.$	Lbs. Liq. /Lb. Vapor	Ft./ Sec.	$Ft.^3$ Hr.	Ft./ Sec.	Lbs./ $Ft.^3$ Hr.
Width of slots of Bubble Caps 0.264 inches Total Slot Area 0.0578 sq. ft.										
					Spacing	20 inches				
0.8	1.2	98.8	76.0	138.0	27.1	0.00067 0.00075	2.26	300	12.8	1700
0.9	2.7	159.0	136.0	203.0	27.1	0.0021 0.0023	3.68	489	20.8	2765
1.4	3.7	205.6	170.0	239.0	27.1	0.010 0.0071	4.75	630	26.9	3570
1.8	5.3	266.0	232.0	298.0	27.1	0.039 0.039	6.15	816	34.8	4625
0.5	0.8	73.4	46.0	119.0	27.5	0.000061 0.000063	1.75	228	9.9	1292
1.4	4.4	242.5	189.0	256.0	27.1	0.013 0.013	5.6	745	31.8	4220
0.5	1.2	78.0	27.0	106.0	27.5	0.000085 0.000083	1.88	262	10.5	1483
0.5	1.2	99.0	39.0	115.0	27.4	0.00063 0.00065	2.34	308	13.3	1744
0.7	2.7	168.2	81.0	142.0	27.3	0.0022 0.0020	3.91	517	22.2	2930
0.7	3.3	215.2	80.0	140.0	27.3	0.011	5.0	661	28.3	3745
					Spacing	18 inches				
0.5	1.1	81.0	187.0	104.0	27.3	0.00036 0.00054 0.00042	1.88	248	10.6	1405
0.9	2.4	143.0	63.4	180.0	27.3	0.0016 0.0021	3.33	439	18.9	2482
0.6	3.0	194.0	66.4	137.0	27.3	0.0042 0.0034	4.5	595	25.5	3370
1.0	3.7	234.0	90.0	164.0	27.3	0.018 0.021	5.46	718	31.0	4060
0.8	4.3	267.0	108.0	174.0	26.8	0.032 0.049	6.2	819	35.1	4630
0.8	4.3	263.0	111.0	183.0	27.0	0.057 0.028	6.11	806	34.6	4570
0.5	0.9	74.0	52.0	139.0	27.3	0.00023 0.00030	1.72	227	9.7	1286
0.6	2.0	131.6	99.0	180.0	27.3	0.0020	3.06	405	17.3	2292
0.9	3.1	187.5	140.0	186.0	27.0	0.014 0.017	4.37	576	24.7	3265
1.4	4.4	243.5	198.0	243.0	26.9	0.020 0.020	5.68	749	32.2	4240

TABLE I.

Dynamic Liquid Level Above Top of Slots	Total Pressure Drop through Plate	Pounds per Hour			Specific Volume of Vapor	Entrainment	Vapor Velocity			
		Vapor into Middle Plate	Overflow from Top Plate	Overflow from Middle Plate			Though Column		Slot	
						Lbs. Liq. /Lb. Vapor	Ft./ Sec.	Lbs./ Ft.² Hr.	Ft./ Sec.	lbs. Ft.² Hr.
In. H_2O	In. H_2O	V_2	O_1	O_2	Ft.³/Lb.					
1.8	5.2	262.0	213.0	312.00	27.0	0.028 0.029	6.11	805	34.6	4570
1.8	5.3	265.0	202.0	308.0	26.8	0.037 0.042	6.17	814	35.0	4600
					Spacing	15.5 inches				
0.5	1.0	70.0	45.0	178.0	27.3	0.00020 0.00020	1.63	215	9.2	1218
0.6	2.0	128.0	94.0	187.0	27.3	0.0034 0.0036	2.98	392	16.9	2220
1.1	3.2	190.0	142.0	197.0	27.0	0.0063 0.0088	4.43	583	25.1	3305
1.4	4.1	225.0	176.0	211.0	26.9	0.049 0.026	5.24	690	29.7	3910
1.7	5.0	258.0	208.0	242.0	26.8	0.063 0.081	6.0	791	34.0	4480
					Spacing	12 inches				
0.4	0.6	61.6	39.0	140.0	27.3	0.00035 0.000306	1.43	189	8.1	1070
0.5	1.9	130.6	90.0	135.0	27.2	0.0138 0.0095	3.02	399	17.1	2260
0.7	2.4	160.2	114.0	135.0	27.1	0.0146 0.0413 0.0267	3.70	491	21.0	2785
1.2	3.5	204.5	149.0	210.0	27.0	0.0855 0.0619	4.69	625	26.6	3540
1.1	4.1	229.2	167.0	203.0	26.9	0.2185 0.0975 0.1080	5.23	701	29.6	3970
1.2	3.9	228.1	87.0	177.0	26.9	0.127 0.151	5.23	700	29.6	3965
1.0	3.3	203.3	75.5	148.5	27.0	0.0567 0.0697	4.67	623	27.1	3530
0.7	2.6	176.9	63.0	123.5	27.1	0.0212 0.02293	4.08	543	23.2	3080
0.6	1.8	134.5	48.0	109.0	27.2	0.0091 0.010 0.0101	3.11	411	17.6	2330
0.5	1.4	111.6	37.0	104.0	27.3	0.00541 0.00835 0.00529	2.58	340	14.6	1925
0.4	0.6	66.0	16.0	86.5	27.3	0.00105 0.00029 0.00014	1.53	202	8.7	1145

TABLE I.

Dynamic Liquid Level Above Top of Slots	Total Pressure Drop through Plate	Pounds per Hour			Specific Volume of Vapor	Entrainment	Vapor Velocity			
							Though Column		Slot	
In. H_2O	In. H_2O	Vapor into Middle Plate V_2	Overflow from Top Plate O_1	Overflow from Middle Plate O_2	Ft.³/Lb.	Lbs. Liq. /Lb Vapor	Ft./ Sec.	Lbs./ Ft.² Hr.	Ft./ Sec.	Lbs./ Ft.² Hr.
					Spacing	31.2 inches				
1.4	3.8	203.3	176.0	271.0	27.0	0.0083	4.67	623	26.5	3530
1.4	3.8	207.5	194.0	271.0		0.0067	4.76	635	27.0	3595
1.4	3.8	207.5	194.0	271.0		0.0059				
1.6	4.5	234.1	221.0	282.0	26.9	0.0055	5.36	718	30.4	4060
1.7	4.8	248.1	229.0	292.0		0.0050	5.69	761	32.2	4310
1.6	4.4	230.8	214.0	281.0		0.0043	5.28	706	29.9	4000
1.7	4.9	251.8	230.0	297.0	26.8	0.0061	5.75	774	32.6	4380
1.7	4.9	251.8	218.0	284.0		0.0053	5.75	774	32.6	4380
1.6	4.3	225.0	192.0	295.0		0.0022	5.14	690	29.1	3910
1.3	3.6	196.2	164.0	253.0		0.0080	4.46	600	25.3	3400
1.4	3.9	212.3	179.0	276.0		0.0063	4.84	650	27.4	3680
1.4	3.9	210.3	180.0	277.0		0.0062	4.80	645	27.2	3650
1.8	5.3	268.4	232.0	285.0	26.7	0.0065 0.0080 0.0086	6.11	825	34.6	4670
1.2	3.3	177.2	144.0	252.0	27.1	0.0014	4.09	543	23.2	3075
1.1	3.0	166.6	115.0	226.0		0.0023	3.83	509	21.7	2880
1.3	3.7	205.7	133.0	242.0		0.0026	4.72	628	26.8	3556
1.0	2.8	159.1	129.0	227.0	27.1	0.0011 0.0013 0.0015	3.67	488	20.8	2765
0.7	1.9	118.0	76.0	171.0	27.2	0.00043 0.00058 0.00061	2.79	359	15.8	2015
1.6	3.7	186.9	163.0	262.0	27.0	0.0018 0.0028 0.00251 0.0023 0.0018 0.0025 0.0013 0.0014	4.3	574	24.4	3250
1.9	5.5	277.8	221.0	300.0	26.7	0.0098 0.011 0.0097 0.015 0.0076 0.013	6.32	853	35.9	4830
Width of Slots in Bubble Cap 0.109 inches Total Slot Area 0.02395 sq. ft.										
1.0	3.3	121.8	94.0	203.0	26.9	0.00054 0.00052 0.00034	2.77	371	37.7	5050
1.0	4.6	179.5	146.0	228.0	26.6	0.0013 0.00075 0.0011 0.0011	4.06	550	55.3	7490

TABLE 1.

Dynamic Liquid Level Above Top of Slots	Total Pressure Drop through Plate	Pounds per Hour			Specific Volume of Vapor	Entrainment	Vapor Velocity			
							Though Column		Slot	
In. H_2O	In. H_2O	Vapor into Middle Plate V_2	Overflow from Top Plate O_1	Overflow from Middle Plate O_2	Ft.³/Lb.	Lbs. Liq. /Lb. Vapor	Ft./ Sec.	Lbs./ Ft.² Hr.	Ft./ Sec.	Lbs./ Ft.² Hr.
0.9	5.3	207.8	163.0	225.0	26.4	0.0013 0.0013 0.0017 0.0017	4.68	639	63.7	8700
.....	.....	290.7	235.0	282.0	26.0	0.0049 0.0056 0.0080 0.0049 0.0066	6.45	893	87.8	12150
					Spacing	18 inches				
0.9	2.5	89.3	61.0	132.0	27.0	0.00022 0.00018 0.00012 0.00027	2.04	273	27.8	3720
1.0	3.6	137.6	122.0	198.0	26.8	0.0035 0.0043 0.0032 0.0031	3.15	423	42.9	5760
0.9	4.4	173.0	136 0	194.0	26.6	0.0048 0.0057 0.0055	3.92	531	53.4	7240
1.0	5.0	187.0	150.0	238.0	26.5	0.014 0.014 0.014 0.014	4.35	592	59.2	8060
0.9	6.1	231.0	171.0	236.0	26.3	0.029 0.027 0.029 0.032	5.27	721	71.7	9820
0.9	6.8	259.0	182.0	268.0	26.1	0.074 0.062 0.063 0.066 0.059	5.86	810	79.9	11030

Effect of Column Vapor Velocity on Entrainment

Figures 4 and 5 show the plot of the original data where the entrainment is plotted against the mass vapor velocity through the column for constant plate spacing. For any given plate spacing the

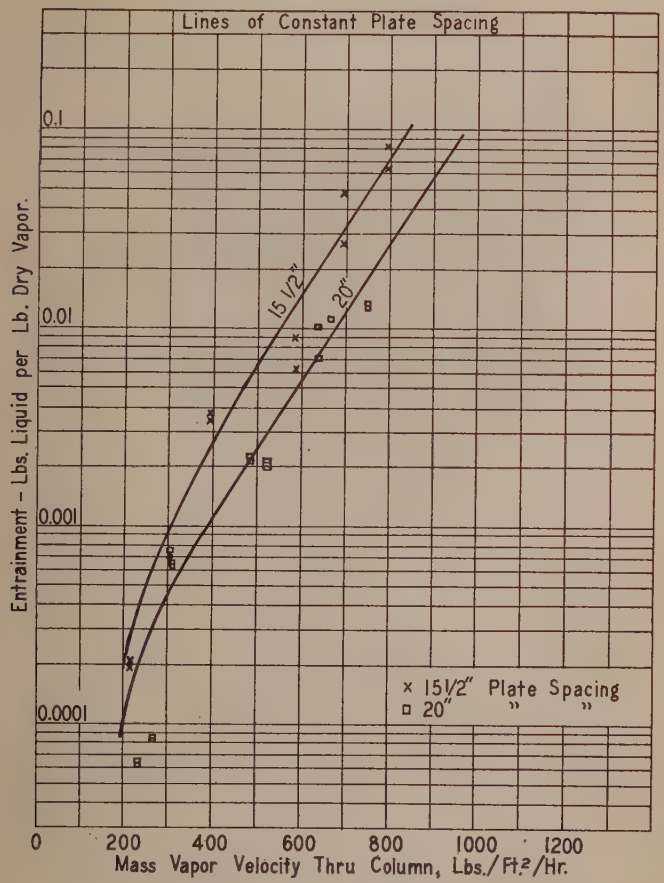

FIG. 5

entrainment increases rapidly with increases in the vapor velocity through the column. For example, with a plate spacing of 31¼", a mass vapor velocity of 400 pounds per square foot per hour through

the main body of the column results in the entrainment of approximately 0.0006 pounds of liquid per pound of dry vapor. With a mass vapor velocity of 800 pounds per square foot per hour, the entrainment is approximately 0.007 pounds of liquid per pound of dry vapor. These facts indicate that doubling the mass velocity through the column results in slightly more than a tenfold increase in the amount of liquid per pound of dry vapor carried from one plate to the one above. It was rather difficult to make accurate determinations of the amount of entrainment corresponding to mass velocities of less than 200 pounds per square foot per hour. All these curves tend to approach each other at lower vapor velocities and fall off rapidly as the vapor velocity is decreased below 200 pounds per square foot per hour. The curves tend to spread somewhat at higher vapor velocities although each curve is approximately a straight line within the range of 300 to 1000 pounds per square foot per hour.

Effect of Plate Spacing on Entrainment

Figure 6 is a plot of the logarithm of entrainment (log E) versus the reciprocal of the plate spacing in inches (1/P). The points shown on this figure were taken from the smoothed curves of Figures 4 and 5. It can be seen that the curves when plotted this way are essentially straight lines. They deviate from a straight line only at plate spacings greater than 20″ and then only when the vapor velocity is relatively low. It is felt that these lines could safely be extrapolated to plate spacings of less than 12″. It can be seen from Figure 6 that the entrainment increases more rapidly for the same increase in plate spacing at higher vapor velocities. At high plate spacings and low vapor velocities these curves deviate somewhat from straight lines.

Effect of Slot Velocity on Entrainment

All the data represented in Figures 4 and 5 were obtained when the individual slot width on the bubble caps was 0.264″. It is apparent that the amount of entrainment is not only a function of the velocity through the main body of the column, but also of the velocity through the slots. The amount of turbulence on the plate and the mass distribution of drop size is obviously a function of the velocity of the vapors as they emerge from the slots. The total quantity of the liquid entrained is a function of the size of the drops, the total number of drops formed, the distance between the plates, and the vapor

velocity through the main body of the column. It could be noticed by visual observation of the column in operation and also from analysis of moving pictures which were taken that many drops formed on the plate and thrown upwards coalesced with others and fell back, whereas other rising droplets were on numerous occasions broken

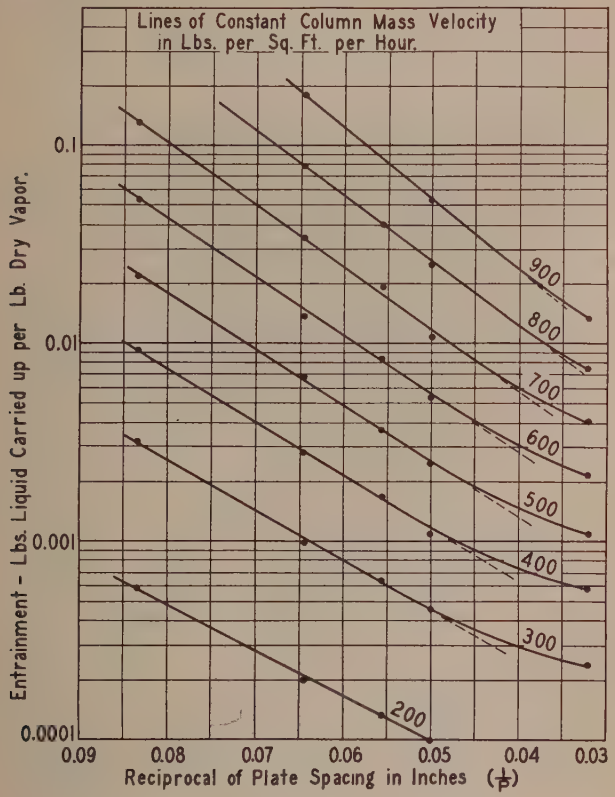

FIG. 6

up and further subdivided. The actual phenomenon is a very complex one and not readily amenable to a mathematical physical analysis. Many drops formed and thrown upwards from the region between the bubble caps were given an initial upward velocity greater than they would maintain in a column of great length where the vapor velocities corresponded to that actually existing in the main body of the column

under the conditions of operation. They were, so to speak, shot out from around the bubble cap and on rising upwards lost some of their velocity. Many of them, being too large to be sustained by rising

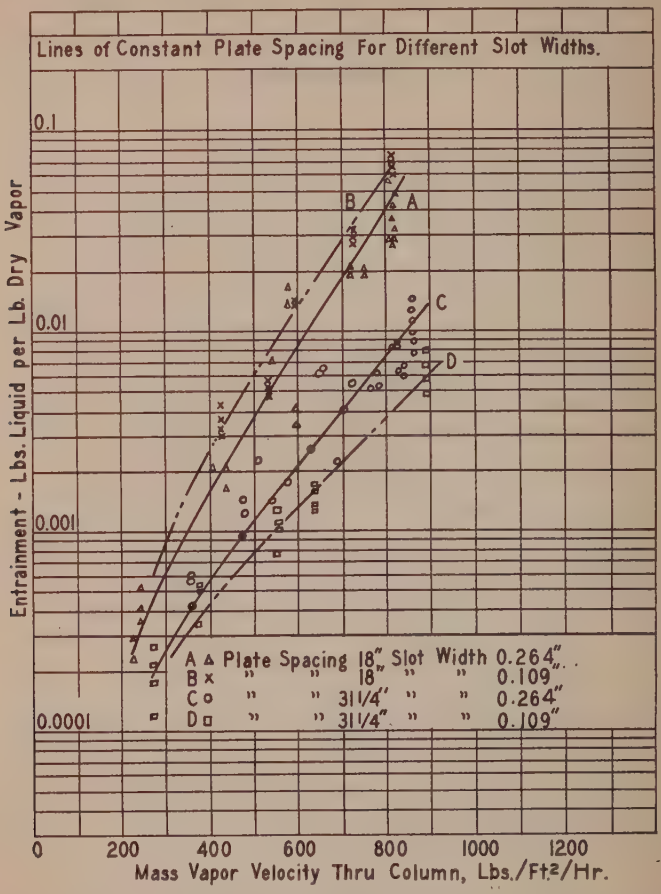

FIG. 7

vapors, began to fall back after reaching the crest of their upward movement. Entrainment as a result of these drops obviously depended upon the distance between the plates.

In order to find out how much effect the slot vapor velocity had on the amount of entrainment, new bubble caps were installed which

were the same in all respects as the ones used previously except that the slot width was reduced from 0.264″ to 0.109″. For the same velocity through the column, the velocity through the smaller slots would be about 2.41 times that with the larger slots. A series of runs was then made with plate spacings of 18″ and 31¼″. The data so obtained are indicated in Figure 7 by curves B and D. Similar curves for the former slot width of 0.264″ and for corresponding plate spacings are indicated by curves A and C along with the original points in each case.

The curves of Figure 7 indicate that for a plate spacing of 18″ the entrainment was somewhat greater for the narrower slot width (greater slot velocity) whereas, at 31¼″ the entrainment was smaller for the narrower slot width (greater slot velocity). Visual observation indicated that the full slot area was being utilized under all conditions and hence the slot vapor velocities were directly proportional to the slot widths. The actual process of drop formation is quite complicated and apparently more or less random. Depending upon the specific conditions of operation, the effective surface of the liquid, which vibrates in a wave-like motion, will extend some distance above the top of the slots. Above this surface large drops or even slugs of liquid will rise several inches and then fall back to the plate. Above this range, some of the drops begin to coalesce and some begin to subdivide when colliding with others. In this space the general streaming is upwards. Observation of the column in operation leads one to believe that the design of the entire plate assembly may account for differences in entrainment of about the order of magnitude indicated by the results obtained from the experiments using these two slot widths. The reason why a higher slot velocity gave more entrainment at 18″ plate spacing and less at 31¼″ plate spacing could probably be explained if mass-drop size distribution data were available for the different conditions. Such data would be difficult to determine and are not now available. The real importance of these data lies in the fact that they prove that slot velocity does not play as important a role in influencing entrainment as do column velocity and plate spacing. This is indicated by the fact that more than a twofold increase in slot velocity, at the most, only doubled the entrainment, other conditions being equal. It was also shown that under certain conditions an increased slot velocity may actually decrease the entrainment. On the other hand, reducing the plate spacing one-half or doubling the column velocity may easily result in a tenfold increase in entrainment.

Effect of the Amount of Reflux on Entrainment

The amount of liquid overflowing plate 2, the one from which the amount of entrainment E was evaluated, is recorded in the data of Table I. The amount of overflow was recorded because it was known that the amount of entrainment was affected by this variable. However, the quantity of overflow does not have as great an effect on the amount of entrainment as some of the other variables studied and therefore no special investigation was made of this factor. It was determined that as this specific column was operated, the order of magnitude of the change in the amount of entrainment brought about by the increase in the overflow from 100 to 300 pounds per hour was approximately twofold. On the other hand, a corresponding increase in the mass vapor velocity, as for example from 200 to 600 pounds per square foot per hour, would produce approximately an hundredfold increase in the amount of entrainment (plate spacing 12″). Since it was known that the amount of entrainment did vary with overflow, it was thought valuable to record the amount overflowing plate 2 which was the one studied. A large rate of overflow has the effect of producing a greater submergence as indicated by the data showing the increase in the dynamic liquid level. When the amount of liquid overflow is small, a portion of the vapors emerges from the slots without ever contacting the liquid and therefore does not have an opportunity to entrain some of the liquid.

Effect of the Surface Tension of the Solution on Entrainment

Since it was known that the surface tension of the solution in the column would affect the amount of entrainment, it was thought desirable to record the surface tension of the relatively dilute sodium chloride solutions which were used in the column. The increase in the surface tension of salt solutions over that of pure water for various concentrations at temperatures from 0° C. to 30° C. is given in the International Critical Tables, Volume 4, page 465. Since the column was operated at approximately 212° to 214° F., these data were not satisfactory. The Sugden* Maximum-Bubble-Pressure method was used to determine the surface tension because it is a method which can conveniently be used to determine the surface tension of liquids at their boiling points. It was found that surface ten-

* Chem. Soc. 121, 858 (1922); 125, 27, 1924.

sion of the liquid on plate 2 varied with the salt concentration, but for all the tests it was within the range of 59 to 64 dynes per centimeter.

Previous experiments on another column with 12″ plate spacing and with complete plate assembly identical to that used in this investigation indicate that the amount of entrainment is appreciably affected by changes in the surface tension of the solution used. A few values are quoted from this previous investigation in order to indicate how sensitive the entrainment is to the surface tension of the solution and the related property, foaming power.

In the first run a strong soap solution was added to the reflux thereby lowering the surface tension of the liquid on each plate. This gave an average value of 41.2 dynes per centimeter for the surface tension at the boiling point of the solution. This represented a lowering of about 30 per cent. from the 63 dynes per centimeter which was the average value for the surface tension when no emulsifying agent was used. In three subsequent runs Emulsopin* was added to the reflux and the surface tension thereby lowered to about 55 dynes per centimeter at the boiling point, therefore corresponding to about a 12 per cent. decrease.

TABLE II

Run	Vap. Vel. Ft. Per Second	Reflux Ratio O/V	Av. S. T. Dynes Per cm.	Av. Ent.	Av. Ent. When S. T. Is 63
1	1.52	0.202	41.2	0.091	0.0
2	5.15	0.46	56.4	0.103	0.08
3	4.5	0.496	54.4	0.091	0.05
4	4.73	0.501	55.3	0.101	0.061

These data are inserted at this point merely to indicate the order of magnitude of the effect on the amount of entrainment which is brought about by changes in the surface tension of a given solution. No extensive attempt was made in this particular research to solve the problem of the relationship of surface tension or foaming power to entrainment. It should be noted at this point that the absolute surface tension of the solution probably cannot be directly correlated to entrainment for various liquid-vapor systems. The surface tension not only affects the size of the drops, but also the foaming power of the solutions. Foulk[6] has done a great deal of work on the surface

*Glyco Products Co., Brooklyn, N. Y.

tension and foaming power of solutions and apparently has come to the conclusion that these two properties cannot be universally correlated. Since both properties affect the amount of entrainment, it does not seem hopeful that complete correlation between surface tension and entrainment for various liquid-vapor systems will be attained.

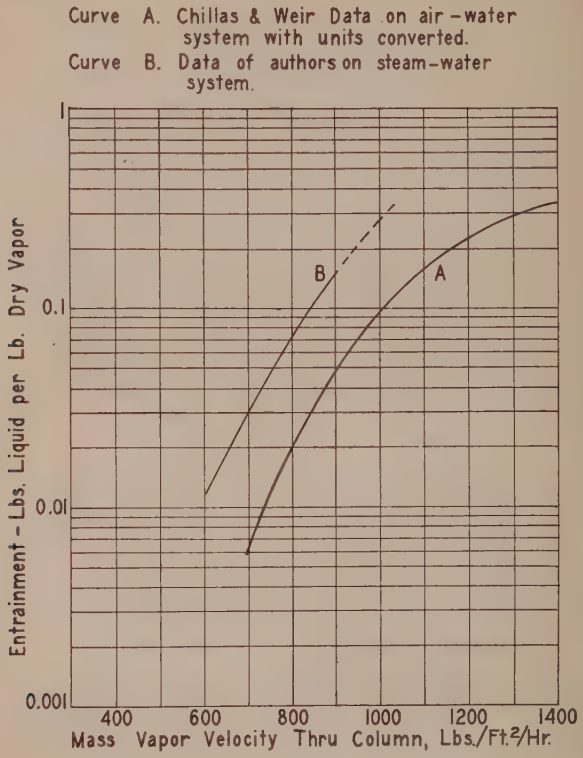

FIG. 8

More fundamental and quantitative data on entrainment are required before this point can be definitely settled. Since the above data do indicate the rather marked effect which the change of surface tension does have on entrainment, it was felt advisable to record the surface tension of the solutions used in this investigation so that they might prove useful for comparative purposes if anyone should thoroughly investigate the relationship between surface tension and entrainment.

Comparison of Results with Work of Other Investigators

A comparison of the data of Chillas and Weir with those of the authors is shown in Figure 8. The upper curve B represents data obtained in this investigation whereas the lower curve A represents the data of Chillas and Weir. There seems to be quite a discrepancy, but it is not as serious as it first looks due to the fact that entrainment is so sensitive to some variables. It has been pointed out that in some cases, for example, that doubling the vapor velocity will increase the amount of entrainment tenfold. The published article of Chillas and Weir does not give sufficient data and details of the plates that they used to give any clue as to why this apparent discrepancy exists. That much difference in the results could possibly be caused by a large difference in slot width, by a different amount of immersion, or by a marked difference in the design of the bubble caps or the plate. It should also be remembered that since they used an air-water system at room temperature, the surface tension of their solutions were higher than they were in this investigation and the density of their vapor was also different from that of the vapor in these experiments. It is the opinion of the authors, therefore, that the apparent discrepancy per se does not indicate a lack of accuracy in the actual determinations of either investigation.

Due to the complexity of the physical process of entrainment, it is apparent that the design of the bubble caps, their relative positions on the plate, and other physical characteristics of the plate assembly will affect the amount of liquid entrained under any given conditions. This fact should also be borne in mind when experimental data on entrainment are being compared. It is for that reason that an attempt has been made in this research to record the complete detailed dimensions of the complete plate assembly and the column proper as well as all the physical characteristics of the system used and the conditions of operations which might conceivably affect the amount of liquid entrained.

Summary

Design of Experimental Laboratory Column:

Since the column which was constructed for and used in this experimental work contained some features which are believed to be new and of possible value to other investigators doing similar work,

a brief description of it and rather complete detail and assembly drawings have been presented.

Effect of Column Vapor Velocity on Entrainment:

The amount of entrainment has been determined for column vapor velocities ranging from 200 to 900 pounds per square foot per hour or 1.5 to 6.5 feet per second, for plate spacings ranging from 12" to 31½". In general, doubling the column vapor velocity results in approximately a tenfold increase in entrainment. Furthermore, the closer the plates are, the greater is the effect of the column vapor velocity.

Effect of Plate Spacing on Entrainment:

Plate spacing and column vapor velocity are about equally important in determining the amount of entrainment under any given conditions. A plot of the log of entrainment versus the reciprocal of the plate spacing for various vapor velocities has been presented. The curves on this figure are nearly straight lines over the range covered and this permits fairly accurate interpolation or extrapolation of the recorded data. As an approximate generalization it can be said that cutting the plate spacing in half will result in about a tenfold increase in entrainment.

Effect of the Amount of Reflux on Entrainment:

The amount of reflux has only a moderate effect on entrainment as compared to plate spacing and column vapor velocity. In this connection it has been pointed out that increasing the reflux from 100 to 300 pounds per hour results in approximately a twofold increase in entrainment.

Effect of Slot Vapor Velocity on Entrainment:

Entrainment is not very sensitive to changes in the slot vapor velocity, other things being equal. The effect of slot vapor velocity is about the same order of magnitude as that of the amount of reflux. Because of the complexity of the physical phenomenon it is not felt safe to attempt a generalization with regard to this variable. It has been pointed out that, under certain conditions, increasing the slot velocity 2.41 times only doubled the entrainment, whereas under other conditions this same increase in velocity actually decreased the amount of entrainment.

Effect of Surface Tension on Entrainment:

Data have been presented which indicate that the surface tension of the liquid does affect the amount of entrainment as would be expected from theoretical considerations. Compared to the other variables which affect entrainment it does not appear as important. It has been pointed out that surface tension affects foaming power, and that these two properties to date have not been satisfactorily correlated. It is therefore believed that a generalized correlation between surface tension and entrainment is as yet impractical.

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Discussion

Discussion Session On "Principles of Chemical Engineering"
(Summarized by T. H. Chilton, Chairman, Sub-Committee on Papers)

Following the presentation of his paper, Dr. Holbrook exhibited a motion picture of the apparatus described while in action. Professor McAdams likewise presented a motion picture illustrating the action of a single cut-away bubble cap at various vapor velocities in a rectangular glass section.

H. O. Chute (written): It appears that the authors of some of these papers have used a system of nomenclature which differs from that familiar in the field of distillation and it would be an advantage if authors would define exactly what is meant instead of employing the "slang" of a particular branch of the industry. Some standardization of nomenclature would certainly be desirable.

No definition was given in the first paper of "equilibrium plates." These seem to be hypothetical compositions for the vapor and liquid are not in equilibrium until the still stops. It is evident that the

liquid which comes through the down-pipes must, when it arrives on the lower plate, have the same composition it had when it left the upper plate. Its composition changes as it passes across the plate and works its way down through the column.

In the discussion of entrainment, the authors appear to think that the spray should be avoided, but actually the drops and spray increase the surface contact and thus the efficiency of separation. The more spray the better, until it passes up by entrainment to the higher plates in too great a proportion.

After all, the designing and building of stills is most successfully done by manufacturers and others who have had considerable experience with using them for the particular purpose desired and who will build one a little bigger than the previous one which works successfully under like circumstances. This formula, while the best to rely on, is limited to those with long experience.

R. B. Chillas, Jr. (The Atlantic Refining Co., Philadelphia, Pa.—written): In reply to Dr. Holbrook's inquiry, the bubble caps employed in the entrainment experiments which we have reported (Trans. Am. Inst. Chem. Engrs., 22 79-109, (1929), were rectangular caps, 3½" wide, 2" high and 15" long with semicircular ends. The lower edge flares outwardly 30° from vertical, and has trapezoidal slots ⅞" high, ¼" wide at the top, ½" wide at the bottom, and spaced ⅞" center to center. These caps were spaced 6" from center to center and mounted over the vapor uptakes with ¼" clearance between the bottom of teeth and the upper face of the bubble plate. (See also Figure 5, in above reference.)

We fully appreciate the value of the data presented by Dr. Holbrook and by Dr. McAdams but must point out that considerable care must be used in applying this to design problems. In columns whose diameter is small in comparison with plate spacing, much of the spray impinges on the walls, which thus act as entrainment separators. (This may account for part of the differences shown in Figure 8 of Holbrook and Baker's paper.)

Many other factors influence the results, such as the size and shape of the space between adjacent bubble caps, the vapor velocity through this space, and whether much of the spray is thrown vertically or with some considerable horizontal component.

Some experiments along the latter line were made to determine the mutual effect of two equal opposing air jets upon their discharge characteristics and spray throwing tendencies. Using 1" diameter jets, with air velocities of 15 to 70 ft./sec., no apparent effect was found until the jets were brought within 3" of each other. At lesser distances, the "discharge coefficient" decreased sharply. Enough was learned from these experiments to indicate that if the vapor jets from opposed bubble caps are not exactly centered upon one another, many of the drops of spray thrown up by such an arrangement apparently have more of a horizontal movement than those from directly

opposed jets. With plate spacing of 15″-18″ or more this may show reduced entrainment. Much more work will have to be done on this interesting subject before we can predict the entrainment under given circumstances.

A. P. Colburn: In connection with the material on entrainment presented at this session, it would be of interest to the members to consult a paper recently presented at the Midwest Meeting of the A. C. S. by R. L. Huntington of the University of Oklahoma and his associates, which confirms the effect of density of the vapor on entrainment and the general effect of plate spacing reported in the present papers.

A. L. Campbell: I would like to inquire if there have been any data obtained on ammonia stills. The work of Parrish is out of date and of little practical value to the present day industry.

SOLUTION CYCLES

By WILLIAM H. SELLEW*

Single component working fluids for heat cycles such as water or mercury for power generation, and ammonia or sulphur dioxide for refrigeration, are generally recognized in engineering practice. But the use of solutions of two or more components in operations including separation and solution is limited in practice almost exclusively to the ammonia-water absorption cycle. Absorption cycles using solutions of many kinds offer a most interesting and promising field of investigation. Because of the wide range in properties, and the additional variables, made possible by solutions over single components as working fluids, results, otherwise impossible, can be attained. The chemical engineer's domain is ever expanding and promises to include heat and power engineering if solutions are employed for these purposes.

Early Work

The operation of the early solution cycles was dependent upon the fact that the vapor pressure of a volatile component from a solution is less than that of the pure liquid component at the same temperature. Apparently Sir John Leslie,[21] in 1810, was the first to make practical application of this phenomenon. He employed, in combination with the air pump previously used in the Cullen vacuum refrigeration machine, a vessel containing strong sulphuric acid for absorbing water vapor evolved at low pressure from liquid, thereby cooling and freezing the water by removal of the latent heat of vaporization.

In 1822 Faraday [1] gave, apparently for the first time, the results of quantitative investigations of the increase in temperature of a boiling solution above that of the boiling pure solvent. The highest temperature attained at atmospheric pressure was with a potassium salt and amounted to 318°F.

* Ann Arbor, Michigan

The early refrigeration machines of the solution or absorption type as first constructed by Carré in France using ammonia, were not entirely practical. In 1867 Rees [21] took advantage of the principle of fractional condensation and developed a machine in which the distillate was nearly anhydrous, thus avoiding the main difficulty of the Carré machines.

The first record we have of utilizing a solution in connection with the production of power is the announcement by Spence,[16] to

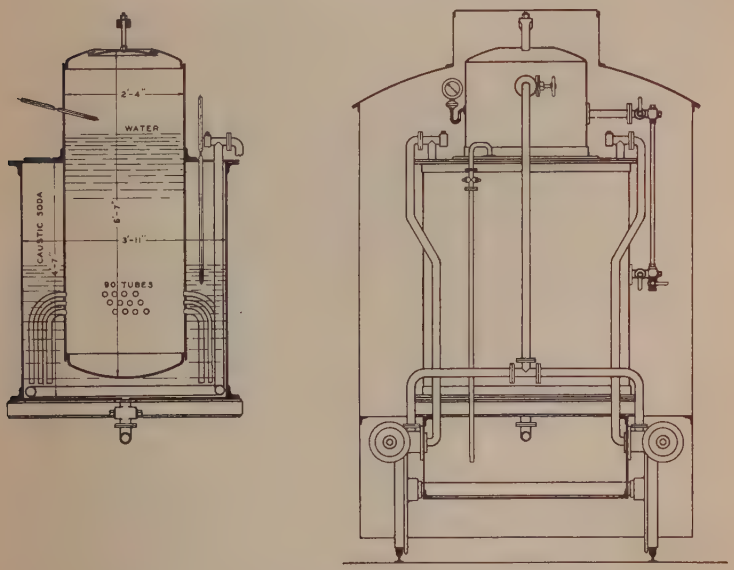

FIG. 1. Honigman Street Railway Locomotive.[13]

the British Association, at its meeting at Exeter in 1869, that the exhaust steam from an engine when liberated at atmospheric pressure (at a temperature of 212°F.) and passed into a saline solution would raise this saline solution to its own boiling point.

A few years later Lamm,[5] a native of New Orleans, was granted a patent on the idea of operating a street car with a steam engine; the engine exhaust being absorbed by a calcium chloride solution which thereby became heated and served to generate fresh steam from water for the engine.

In 1874 Spence's son,[16] following in the footsteps of his father, proposed to employ the heat of waste steam as a substitute for fuel. He brought the exhaust steam (at 212°F.) from an engine, into contact with a solution of caustic soda that had a boiling temperature substantially greater than that of water. The temperature of the solution was raised to 375°F. and the heated solution was circulated through pipes in an ordinary boiler for the purpose of generating steam in the place of heat derived from fresh fuel.

Early in the next decade Honigmann,[13] the proprietor of extensive chemical works at Aix-la-Chapelle in Germany, working along apparently independent lines, built several locomotives operated on the solution principle.[17] Fig. 1 illustrates one of the smaller machines of the Honigmann type as described by Riedler.[13] The so-called Honigmann fireless locomotive, was commented upon extensively in the technical press of Germany as well as in that of France, England and the United States.

It was quite generally recognized, however, that the thermal efficiency of the process was relatively low. It was stated for example, that the boiling down of the solution required more coal than the evaporation of water does under equal circumstances.[18]

The concentration means employed by Honigmann were inefficient. His real contribution was largely confined to demonstrating the entire feasibility of regenerating, on a commercial scale, the heat of the exhaust to make fresh steam. In a patent [3] granted in 1886, he proposed to add a fire box to his "fireless" locomotive and concentrate the solution under the same pressure as that employed in the cylinders. This procedure offered a possibility of increased thermal efficiency over his other designs which had concentrated at atmospheric pressure.

D'Equevilley-Montjustin in 1911 suggested [9] the use of solutions with a steam power plant for the propulsion of submarine vessels which generated driving steam in a fired steam boiler during surface travel, and in a hot water boiler when running submerged. The hot water boiler, first used by Nordenfelt, obviously provides only a very limited submerged radius, and Montjustin's idea was to use a solution boiler which would act as a regenerator during submerged travel. The arrangement appeared favorable [22] compared with a Diesel operated boat with storage batteries, when submerged, but less favorable for surface operation.

The Basic Solution Process

All cycles are composed of processes. The basic process peculiar to solution cycles is a thermo compression process, shown in its elemental form as I in Fig. 2, All solution cycles whether they be simple or complicated include, in one way or another, this elemental thermo-compression process.

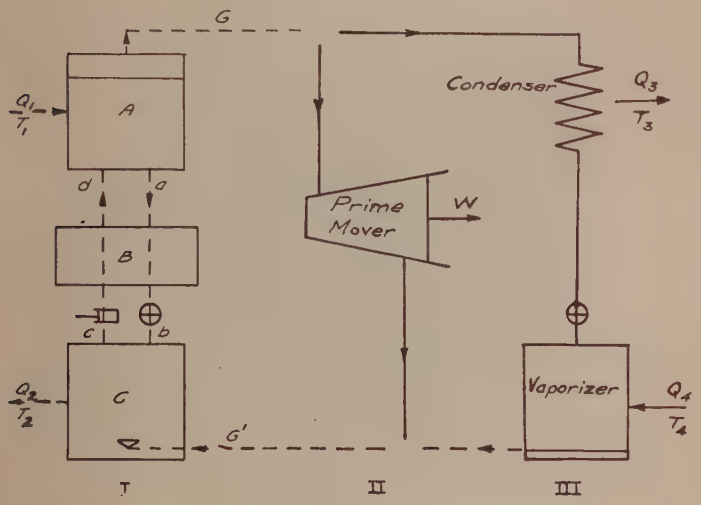

Fig. 2. Elementary Solution Cycle.
I.—Basic Solution Thermo-Compression Process; II.—Power Process; III.—Refrigeration Process.

The concentrator A is supplied, at temperature T_1, with the heat Q_1 which serves to vaporize solvent G, the high pressure vapor, from the solution in A. The absorber C absorbs the low pressure vapor G', with the evolution of heat Q_2 at a temperature T_2 which is less than T_1 but greater than that at which G' will condense. The heat exchanger B serves to preheat the dilute solution pumped from the absorber C to the concentrator A and to cool the concentrated solution flowing from concentrator A through the pressure reducing valve to the absorber C.

In order to complete the cycle the high pressure vapor G may be passed through a conventional prime mover II for the production of

work, and the vapor G′ supplied from the engine exhaust, or if employed with a refrigeration process III in a refrigerating cycle the vapor G may be condensed by rejection of heat Q_3, and, at a lower pressure and temperature, vaporized by the absorption of heat Q_4 to supply the low pressure vapor G′.

The heat exchanger B, introduced in 1908 by Schneevogl,[14] is of obvious importance to the efficient operation of the process.

The resorption cycle of Osenbrück, described by Merkel and Bošnjaković,[8] consists of two such basic processes arranged as shown in Fig. 3. The process at the left is identical with that of Fig. 2

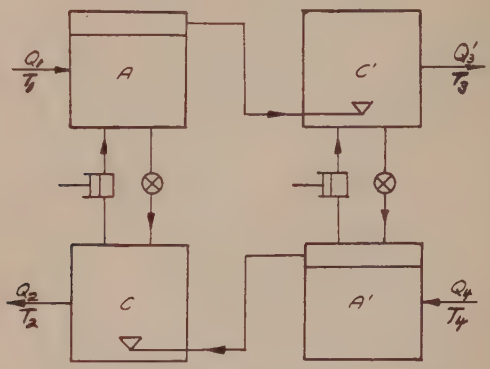

Fig. 3. Resorption Solution Cycle of Osenbrück.

and uses a more concentrated solution than the process on the right which consists of an absorber C′, which absorbs the vapor from concentrator A, and a low pressure concentrator A′ which is operated by heat Q_4 at the refrigeration temperature. The vapor from the low pressure concentrator A′, is then absorbed in the absorber C of the left hand process.

The cycle of Pape [11] shown in Fig. 4 serves to illustrate the conventional solution power cycle composed of the basic solution thermocompression process but without heat exchange, combined with a prime mover and with a Rankine cycle. The concentrator *a* absorbs heat Q_1, giving off the high pressure vapor supplied to the prime mover *f* and the hot concentrated solution circulated through the water heater, to the absorber *c*. Low pressure vapor bled from the prime mover is absorbed into the solution at *b* in absorber *c*. The heat

Q_2 so generated is absorbed by water to generate high pressure steam, which is fed to the prime mover f through line e. The dilute solution is pumped by k to concentrator a for reconcentration.

The quantity of steam bled into the solution through b is equal to that evaporated in a, and the quantity vaporized in coil d and fed to prime mover through e is equal to that condensed in g and pumped through the water heater to be vaporized in d. The basic solution thermo-compression process is, therefore, combined with a prime mover to constitute a heat power cycle a, f, b, c, k, a for the volatile component and a, i, c, k, a for the solution. The heat Q_2 rejected

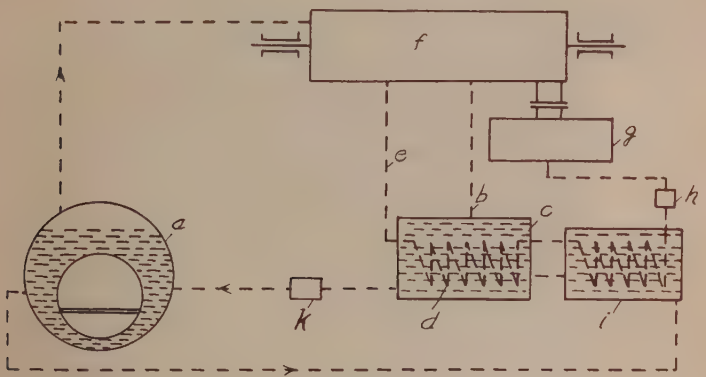

FIG. 4. Power Solution Cycle of Pape.

by the solution thermo-compression process from the absorber is used as the heat source for vaporizing or boiling water in an ordinary Rankine power cycle d, e, f, g, h, d, in an equivalent manner to that used in the combined mercury water power-cycle, but with the solution cycle substituted for the mercury cycle.

The pressure transformer, Fig. 5, suggested by Koenemann for raising the pressure of exhaust steam, was commented upon in this country by Marks [6] in 1927. This pressure transformer is composed of the basic solution thermo-compression process of Fig. 2, to which a water boiler has been added to utilize the heat Q_2 rejected by the absorber of the thermo-compression process. The heat Q_1 is added by the condensation of high pressure steam in a coil located in the concentrator A. Vapor G, at lower pressure, leaves the con-

centrator, is combined with vapor produced in the water boiler from the heat Q_2 generated in the absorber C, and put to the desired use. The source of the vapor G' which is absorbed into the solution in the absorber is the low pressure exhaust steam. The steam generated in the concentrator is equal in quantity to that supplied G' to the absorber.

An additional quantity of steam is generated in the water boiler which absorbs heat from the absorber C. This additional steam is

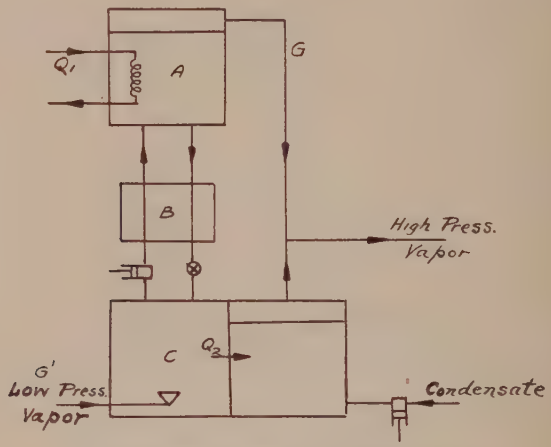

FIG. 5. Koenemann's Solution Thermo Compressor.

roughly equal in quantity to high pressure steam condensed in evaporator A, provided the water feed is at the boiling point of the water in the boiler.

Fundamental Principles

The fraction of heat energy which may be converted into work or available energy in a reversible cycle is given by the well-known expression developed by Carnot.

$$\text{Efficiency of conversion} = \frac{T_1 - T_2}{T_1} \qquad (1)$$

Where T_1 is the absolute temperature at which heat enters the cycle.

T_2 is the absolute temperature at which heat leaves the cycle.

Once the two terminal temperatures T_1 and T_2 are fixed, the maximum percentage conversion of heat into work is also fixed, but this maximum conversion can be reached only under certain very definite ideal conditions. These conditions are three in number.

1. All of the heat that is received by the system that is converting heat into work must be received at T_1. No heat can be allowed to enter at any lower temperature.

2. All of the heat that leaves the system must leave at the temperature T_2. No heat must be allowed to leave at a higher temperature.

3. Every step or process in the operation or cycle must take place reversibly. This requirement is somewhat more difficult to visualize and much more difficult to approach in practice than the other two, as it rules out friction, throttling, flashing, the addition of a cool fluid to a warmer one, temperature heads in heat transfer and all other operations that do not take place under equilibrium or reversible conditions. Although this requirement can be approached, it is impossible of complete realization in any practical operation.

These three requirements are necessary and sufficient for realization of the Carnot efficiency. It is not necessary to postulate any particular type of equipment, any particular kind of cycle, or any particular working substance. Within the system other forms of energy may be involved, such as electrical energy, or chemical energy, provided only that these three requirements are met.

In the Rankine (steam engine) cycle using superheated steam, the heat enters the cycle largely at the saturation temperature, or the temperature at which the water vaporizes. The heat in the superheat is a relatively small part of the total heat entering the cycle. In order to raise the saturation temperature increased pressures as high as 2000 to 3200 lbs. per sq. in. are being used. By the use of aqueous solutions, all of the heat enters the cycle at the temperature of superheated steam, because the vapor formed by boiling a solution is, per se, "superheated" i.e. at a temperature above boiling water at the same pressure. Furthermore the solution may be so chosen as to have a high boiling point at moderate pressures thereby gaining the efficiency of high pressure cycles or of combined mercury-steam cycles, without the troubles of high pressures, or mercury boilers and prime movers.

The use of solution cycles makes possible the fullfillment of the

first two conditions for attaining the Carnot efficiency in a more flexible and convenient manner than can be otherwise accomplished. It remains, therefore, only to limit the irreversible processes within the cycle to attain an efficiency that will approach the Carnot efficiency as calculated from the two terminal temperatures. By proper heat exchange, bleeding of prime movers and other devices not possible to the one component cycle, irreversible processes can be reduced to a minimum or as far as economically justified.

For heating and cooling operations heat Q_1 supplied at a high temperature T_1 to one process which rejects heat Q_2 at a lower temperature T_2 may be used for operating a second process which absorbs heat Q_4 at a low temperature T_4 and rejects as heat Q_3 the heat Q_4 plus the available energy b from the first process at a higher temperature T_3.*

An energy balance around such an operation clearly indicates

$$Q_1 + Q_4 = Q_2 + Q_3 \tag{2}$$
$$Q_1 - b = Q_2$$
$$Q_3 - b = Q_4$$

But, more important, if the operations are conducted in a reversible manner so that Equation (1) may be applied

$$Q_1\left(\frac{T_1 - T_2}{T_1}\right) = \left(\frac{T_3 - T_4}{T_3}\right)Q_3$$
$$\frac{Q_3}{Q_1} = \left(\frac{T_1 - T_2}{T_1}\right) \times \left(\frac{T_3}{T_3 - T_4}\right) \tag{3}$$

Equation (3) expresses the ideal (Carnot efficiency) coefficient of performance for a solution heating cycle when Q_2 is not available for heating.

$$\frac{Q_3}{Q_1} = \frac{\text{heat delivered for heating}}{\text{heating supplied for operation}}$$

*In Figure 2 Q_2 becomes Q_3, T_2 becomes T_3 and Q_3 becomes Q_2 and T_3 becomes T_2 according to the nomenclature used in these relationships applicable to heating or refrigeration cycles.

Similarly

$$Q_1\left(\frac{T_1-T_2}{T_1}\right)=\left(\frac{T_3-T_4}{T_4}\right)Q_4$$

$$\frac{Q_4}{Q_1}=\left(\frac{T_1-T_2}{T_1}\right)\times\left(\frac{T_4}{T_3-T_4}\right) \qquad (4)$$

Equation (4) expresses the ideal coefficient of performance for a solution refrigerating cycle.

$$\frac{Q_4}{Q_1}=\frac{\text{heat absorbed for refrigeration}}{\text{heat supplied for operation}}$$

If T_2 is the same as T_3 as is frequently the case, the heat quantity Q_2 is added to Q_3 for the heating operation, and the coefficient of performance becomes

$$\frac{Q_3+Q_2}{Q_1}=\frac{Q_1+Q_4}{Q_1}=1+\frac{Q_4}{Q_1} \qquad (5)$$

$$\text{or C.P.}_{\text{Heating}}=1+\text{C.P.}_{\text{Refrigeration}} \qquad (5a)$$

In the elemental refrigeration cycle shown in Figure 2, under the same conditions ($T_2=T_3$), the ideal coefficient of performance is

$$\frac{Q_4}{Q_1}=\left(\frac{T_1-T_2}{T_1}\right)\times\left(\frac{T_4}{T_2-T_4}\right) \qquad (6)$$

If, as a very rough approximation, the solution is assumed to follow the Ramsey and Young[12] Rule

$$\frac{T_S}{T_W}=\frac{T_1}{T_2}=\frac{T_3}{T_4}=\frac{T_2}{T_4}=k \text{ (a constant)} \qquad (7)$$

where T_S = absolute boiling point of solution
T_W = absolute boiling point of pure volatile component at the same pressure

Then by substitution from Equation (7), Equation (6) becomes

$$\frac{Q_4}{Q_1}=\frac{1}{k} \qquad (8)$$

Although this expression is not rigorous for any known solution it helps to clarify the relationships between the coefficient of performance in elemental refrigeration cycles such as Fig. 2, and the properties of the solution used. In most cases k is greater than unity

and the coefficient of performance for the simple refrigeration cycle using such a solution must be less than unity. If, however, a solution is employed for which T_s/T_w is less at low pressure than at high pressure a higher coefficient of performance can be obtained because T_1 the temperature of heat input is thereby raised. Equations (4) and (5) show that, for constant T_2, T_3 and T_4, high coefficients are dependent upon high temperatures of heat supply (T_1). Therefore any convenient type of solution may be used to attain high efficiency provided the cycle is so constructed as to absorb heat at a high temperature (T_1) regardless of the vapor pressure characteristics of the solution used.

The possibility of high temperature heat input with all of the heat entering the cycle at the maximum temperature is a most important characteristic of solution cycles which has been apparently neglected until very recently.

This was early apparent to the writer who some years ago discussed the question with the late Dean Goss and with Professor Marks. Shortly thereafter Merkel published his important work[7] on two component mixtures in steam technology, in which he called attention to the significance and importance of high temperature heat input upon the efficiency of the solution cycle.

Present State of Development

In 1930 Koenemann[4] described a solution power cycle which employed ammonia as the solvent, and zinc chloride as the solute. It is substantially the cycle shown by Fig. 4 except that turbine stage *ab* is replaced by a turbine which operates on ammonia vapor. The cycle was commented upon in favorable terms by the technical press of this country[20] and abroad.[19]

The ammonia vapor in this proposed operation is evolved by the decomposition of the ammoniacate and becomes once more recombined in its original form after having performed work.

$$ZnCl_2 \cdot 2NH_3 \rightleftarrows ZnCl_2 \cdot NH_3 + NH_3$$

The initial pressure is 100 lbs. sq in. abs. in the ammonia vapor stage and 300 lb. sq. in. abs. in the steam stage. Heat enters the cycle at 896° F. which is comparable with the upper temperature used in the mercury vapor power cycle.[10]

It would appear that, if the high temperature input of heat required for an efficient operation of the solution cycle can be obtained with an aqueous solution, some advantage may lie in the operation throughout of steam turbines and the use of the more stable steam vapor, which is less subject to decomposition at 900°F., than is ammonia vapor.

Altenkirch has greatly improved the ammonia-water solution cycle for refrigeration purposes. His recent cycle[2] in operation in Ger-

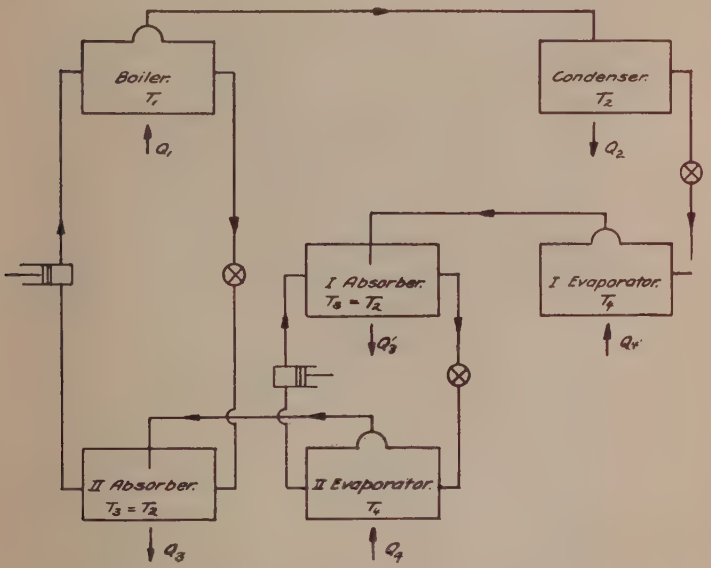

FIG. 6. Refrigeration Solution Cycle of Altenkirch.

many (Fig. 6) takes advantage of the resorption principle (Fig. 3) enunciated by Osenbrück in 1913. Its main claim to our attention, however, lies in its ability to utilize a higher elevation of boiling point of the solution in the basic process at the left of the cycle. This is possible because the saturated temperature of the vapor to absorber II is considerably below the refrigeration temperature. In this cycle the pressure in the various vessels is indicated by their vertical position in the figure, the two absorbers and condenser operate at the same temperature T_2 or T_3 and the two evaporators at T_4.

It is stated by Gompertz and Niebergall [2] that the coefficient of performance of the ammonia-water cycle illustrated in Fig. 6 is, over

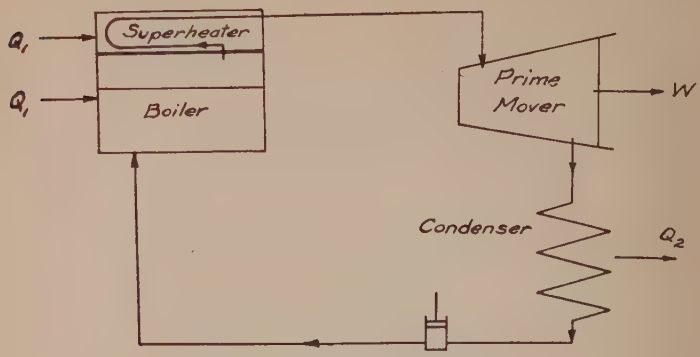

Fig. 7a. Rankine Power Cycle.

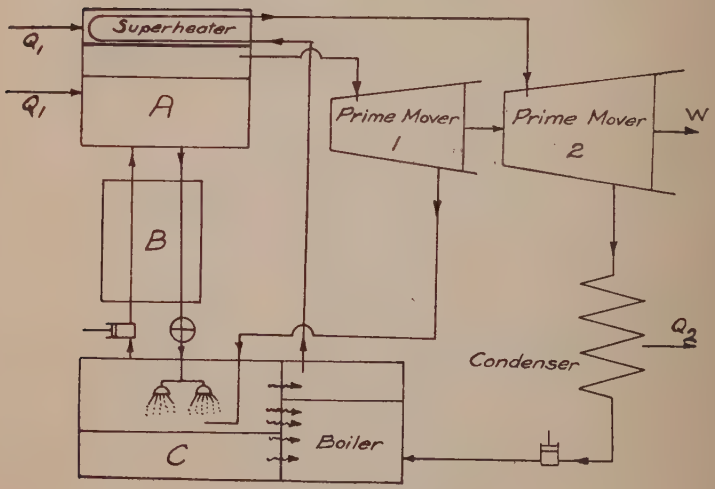

Fig. 7b. Simple Solution Power Cycle.

the ordinary range, more than twice that of the simple ammonia absorption cycle as illustrated in Fig. 2. Over other ranges or with other working fluids this would not be true in all cases.

Outside of Germany little actual commercial development has taken place. Even there the fundamental principles for obtaining high efficiency in solution cycles have only recently been appreciated and the most promising means of attaining high efficiency not yet disclosed.

Comparative Results

The following results calculated from the best available data on the properties of sodium hydroxide solutions indicate the promising results obtainable from simple solution cycles. The limited data available in the literature and from our own experimental work confirm the essential accuracy of the calculations. For convenience and clarity the flow diagrams are given with each comparison.

Fig. 7a represents a simple Rankine cycle which is to be compared with a simple or basic solution steam power cycle (Fig. 7b). For example the solution cycle is considered as using caustic soda solutions of 60% concentration in the concentrator A and 55% concentration in the absorber C. The flow of solutions and vapor is clear from the figure in view of previous discussion. Table I gives a summary of operating conditions and a comparison of the efficiencies of these simple cycles after making allowance for temperature drop in heat exchangers.

TABLE I

	Rankine Steam Cycle-Figure 7a	Solution Steam Cycle–Figure 7b
Maximum Cycle Temperature	487° F.	487° F.
Minimum Cycle Temperature	212° F.	212° F.
Temp. steam to prime mover	487° F.	487° F. to 1 and to 2
Pressure of steam to prime mover	125 lbs. per sq.in. abs.	125 lbs./sq.in. to 1 77.7 lbs. to 2
Pressure of exhaust steam	14.7 lbs.	24 lbs. from 1 14.7 lbs. from 2
Quality of exhaust steam	94%	97% from 1 98% from 2
Heat to cycle (boiler and superheater) per lb. 125 lb. steam	1089 B.t.u.	1403 B.t.u.
Work obtained from prime movers (85% Eff.)	148 B.t.u.	261 B.t.u.
Efficiency of Conversion	13.6%	18.6%

This comparison indicates a gain in the efficiency of conversion of 37%, i.e. for the same heat energy supplied to the cycle 37% more work will be obtained from the solution cycle. This gain in efficiency

is due entirely to the fact that over 92% of the total heat supplied to the cycle is absorbed by the boiling solution in the concentrator at a constant temperature of 487°F., corresponding to 125 lbs. per sq. in. pressure, while in the Rankine cycle, 80% of the total heat is absorbed by boiling water at 344°F. corresponding to 125 lbs. per sq. in., 13% from 212°F. to 344°F. in heating the feed water and the balance between 344°F. and 487°F. in superheating the steam. The steam evolved from the solution is at 487°F. and 125 lbs. per sq. in. and therefore already "superheated."

By further expanding the steam in the Rankine Cycle of Fig. 7a to 0.5 lb. per sq. in. an efficiency of 26.1% is attained in place of 13.6% corresponding to atmospheric exhaust. In comparing such an efficiency with that of the solution cycle of Fig. 7b it will be noticed that by making the exhaust 0.5 lb. per sq. in. from both prime movers 1 and 2 and raising the pressure of the steam supplied to prime mover 2 from 77.7 lb. to 125 lb. per sq. in., a solution of greater concentration may be used (which will give a higher elevation in boiling point) and the performance of the solution cycle correspondingly improved. Owing to the limited data available on the thermodynamic properties of such solutions, particularly in the concentrated region, accurate estimates of the operating conditions cannot be made at present, but it appears that the relative gain in the solution cycle (Fig. 7b) will be of the same order of magnitude as that in the Rankine cycle (Fig. 7a). If the maximum operating pressure is increased, the efficiency of each cycle is likewise increased due to the increase in temperature of heat input (T_1).

Table II gives a similar summary of operating conditions for the solution thermo-compression process of Fig. 2 applied to air conditioning operations.

Since the solution thermo-compression unit requires heat at only 161°F. it may be operated with steam at atmospheric pressure or less as a source of heat (about 7.7 lbs. per sq. in. abs. is the minimum allowing for 20°F. temperature drop). Operated in such a manner about 85 lbs. of steam at 7.7 lbs. pressure are required per hour for a 5 ton unit.

Modern efficient steam jets using steam at 70 lbs. per sq. in. abs. (303°F.) and working over the same pressure limits (corresponding to 40°F. and 90°F.) require about 750 lbs. of steam per hour for 20 tons (240,000 B.t.u. per hr.) refrigeration, which is a coefficient

of performance of 0.285. Allowing substantially the same efficiency for a 5 ton unit, the steam jet requires about 190 lbs. of steam at 70 lbs. pressure as compared with 83 lbs. of steam at about one-half atmospheric pressure for the simple basic solution thermo-compressor. Operation of the jet requires condensing capacity for about 250 lbs. of steam per hour as compared with about 60 lbs. per hour from the simple basic solution cycle.

TABLE II

Operating Conditions For Refrigeration Cycle of Fig. 2 using Caustic Solutions as Suggested by Morris

	Temperature °F.	Pressure Lbs. per sq.in.	Concentration Wt. % NaOH
Concentrator A	161	0.6980	50
Concentrated Solution leaving heat exchanger B	105	0.6980	50
Condenser	90	0.6980	0
Vaporizer	40	0.1217	0
Absorber C	90	0.1217	45 (B.P. 97° F.)

Heat required Q_1 = 81,680 B.t.u. per hr.
Heat absorbed Q_4 = 60,000 B.t.u. per hr.
Coefficient of performance = 0.735

With the improvements described in the following paragraphs the efficiency and operating range of the solution cycle may be extended with much more favorable results.

*Multiple Effect Solution Cycles**

As has been indicated the efficiency of the operation depends upon the absorption of heat into the cycle only at a high temperature. Fig. 8 shows a fundamental modification in the solution cycle which enables the cycle to absorb heat at a higher temperature without in any other way disturbing the operating conditions. This method has not been previously suggested and is most promising as a flexible means of improving the efficiency and extending the range of solution cycles.

By increasing the pressure on the additional concentration A′ so that the vapor therefrom has a sufficiently high temperature of con-

* The operations discussed in this section are covered by patent applications in the U. S. Patent Office.

densation to serve as a source of heat for the concentrator A, additional concentrated solution may be prepared in A′ for dilution in C with corresponding increase in high pressure vapor generated in the boiler, without the absorption of a much greater quantity of heat

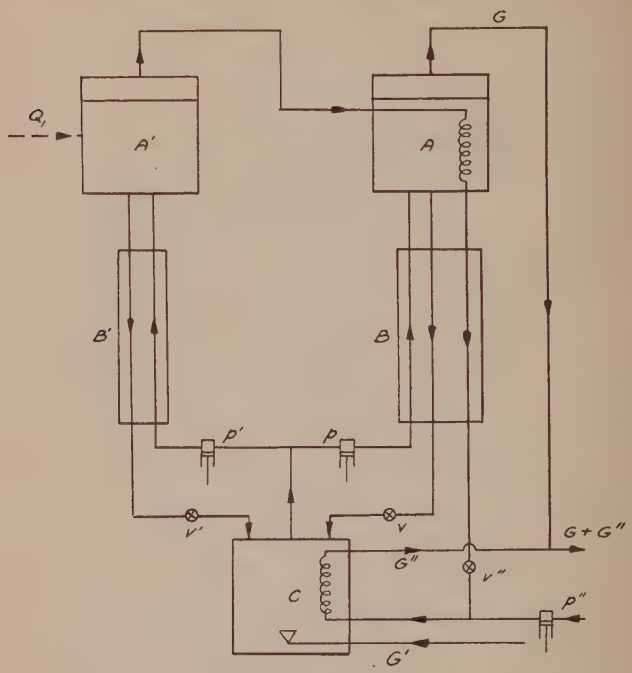

Fig. 8. Solution Thermo Compressor incorporating Double Effect Concentration with Single Effect Absorption.

in A′ than was formerly supplied to A. But the heat is absorbed at a higher temperature.

In a cycle such as Fig. 8 using 60% caustic soda in the concentrators and 55% solution in the absorber, 800 B.t.u. at 492°F. supplied to concentrator A′ which operates at 131 lbs. per sq. in. will compress one lb. of steam from 4 lbs. per sq. in. pressure to 15.9 lbs. per sq. in. A steam jet supplied with steam at 131 lbs. pressure and 492°F. generated in a boiler from feed water at 70°F. will require

about 3700 B.t.u. on the basis of 3 lbs. of activating steam per lb. of low pressure steam, more than 4½ times as much heat as for the solution thermo compressor. The limited data available on operation of efficient steam jets under these conditions indicate a considerably higher steam requirement than has been used in the comparison above, which is more than fair to the steam jet.

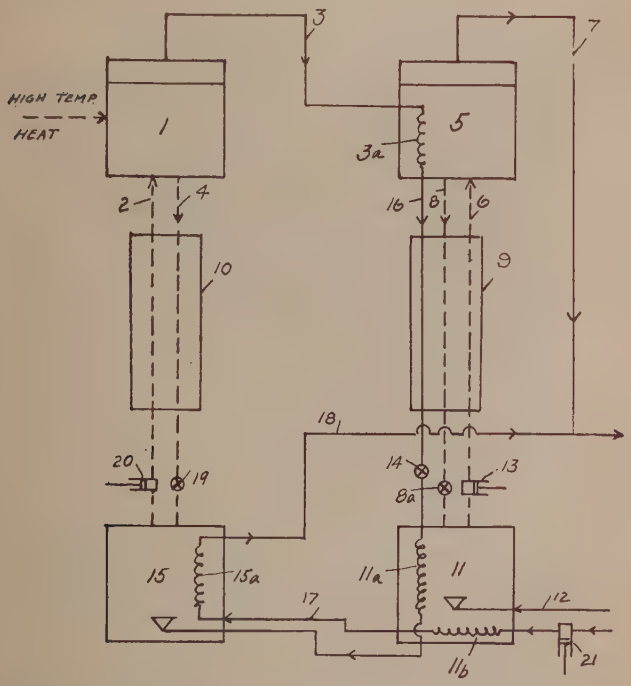

Fig. 9. Solution Thermo Compressor incorporating Double Effect Concentration and Absorption.

Multiple effect may be used, not only for increasing the efficiency by increasing the temperature at which heat enters the cycle, but also for extending the range of operation as for increasing the compression ratio in the manner indicated in Fig. 9. The only essential difference between the cycle shown in Fig. 9 and that of Fig. 8 is in the addition of an absorber in second effect to extend the range of

compression. Representative operating conditions are given in Table III.

TABLE III

Representative Operating Conditions for Fig. 9

	Temperature ° F.	Pressure Lbs./sq.in.	Concentration Wt. % NaOH	Relative Weights
Concentrator 1	500	151	60	
Solution 19	259	151	60	
Concentrator 5	339	18.9	60	
Condensate from 3a	359	151	0	
Absorber 11	179	1	55 (B.P. 183°F.)	
Condensate 14	194	151	0	
Solution 8a	194	18.9	60	
Steam 11a	160	4.74	0	
Absorber 15	244	4.74	55 (B.P. 248°F.)	
Steam 15a	225	18.9	0	
Steam 3	500	151	0	1.28
Steam 12	102	1	0	1
Water 21	70	18.9	0	1.48
Steam 7	339	18.9	0	1
Steam 18	225	18.9	0	1.48

Heat Requirements

To deliver 1 lb. of steam at 18.9 lbs. per sq.in. ..... 710 B.t.u.
To compress 1 lb. of steam from 1 lb. to 18.9 lb. per sq.in. ..... 1760 B.t.u.

If an attempt were made to use a steam jet for this compression ratio of 18.9, two stages would be required and the consumption of steam at 150 lbs. per sq. in. would be about 20 lbs. requiring about 25,000 B.t.u. as compared with 1760 B.t.u. in the double effect solution cycle. Except over small compression ratios recompression of process vapors with jets has not proven economical.

With the use of multiple effect concentration and absorption as suggested in Fig. 9 it is clear that the solution thermo compressor can easily and economically attain high compression ratios, which are entirely impractical by other methods.

A compression ratio of 19 is entirely out of the question with steam jets unless used in two stages and with enormous consumption of steam. Ten stages in a centrifugal compressor are required for compressing low pressure water vapor through a compression ratio of 6 and no centrifugal compressor has yet been developed to operate over a compression raito of 19.

Clearly the use of multiple effect concentration and absorption in solution cycles offers a most efficient and flexible means of operating heat cycles.

There are many modifications and extensions of these principles which make the application of solution cycles to power generation, heating, refrigeration, air conditioning and thermo compression of process vapors, promising.

One feature in particular appears most interesting, namely the efficient storage or transportation of large quantities of available energy in the form of concentrated solution and pure solvent. The chemical energy stored in such a system may be made instantly available by means of a solution cycle, and yet may be stored indefinitely or transported through uninsulated lines without loss of energy.

By the use of a suitable cycle, and heat exchangers the dilute solution supplied at atmospheric temperature to a concentration plant may be converted into concentrated solution, and solvent, which is also made available at atmospheric temperature for immediate use or for storage without loss, so that the concentrating plant may operate at constant load with maximum efficiency throughout the 24 hours, and fluctuation in the load met by the storage of solutions and solvent.

It has been estimated on the basis of a 300,000 K. W. station of six 50,000 K. W. units that the original cost of a solution cycle central power plant would be about the same as that of a modern steam plant because of the reduced capacity of the concentrating units made possible by this storage feature. Therefore substantially all of the savings made by the greater efficiency of the solution cycle plant, which can probably be made comparable with that of the combined mercury water cycle, represent a net gain or profit.

Conclusions

The intensive development of one component cycles has reached such a stage of perfection that consideration should now be given to the broader possibilities of the solution cycle. Although the immediate costs in obsolescence of present equipment may delay the commercial application of solution cycles to central power stations, new and important industries such as air conditioning and cooling of buildings offer a profitable field for the commercial development of solution cycles for isolated stations, or for central stations for heating, air conditioning and cooling office buildings, factories or residences.

Practical problems must, of course, be solved. But present chemical engineering practice in the successful evaporation, transportation and handling of concentrated solutions points the way and promises no serious difficulties.

If such development is undertaken on a large scale it may contribute to that new industry of the next era of prosperity which is just around the corner.

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Discussion

G. G. Brown (preceding presentation of the paper): Mr. Chairman, Members and Guests of the Institute—Mr. Sellew wishes me to convey his regrets at being unable to attend the meeting due to health conditions. I shall do my best to tell the story of "Solution Cycles." About the only operation which is not at present conducted in a commercial manner is the absorption of the vapors in the solution, so that the chemical engineer is in a position to treat these cycles more or less from his past experiences from an engineering standpoint. Caustic soda, from many standpoints, is a promising material, and Professor McCabe, working with Mr. Sellew has prepared charts which give the thermal properties of the caustic soda solutions so that with the combinations of these charts and the steam tables, it is possible to compute the operation of these cycles.

Chairman Marshall: Professor Sellew's paper is now open for discussion and I am sure Professor Brown will be glad to answer any questions.

A. M. Selvey (The Detroit Edison Company, Detroit, Michigan—written): The author has presented an interesting discussion of the history and advancement of the solution cycles from the point of view of the chemical engineer but apparently has understated the problems of the fabricating and operating engineer. There remain many sufficiently-large problems to tax also the ingenuity of the chemical and metallurgical research workers before the increase in thermal efficiency can be economically attained in reality. The materials for the solution cycles are very corrosive to iron and steel, especially at the temperatures of 800-900 F. quite common in power-plant practice.

The advantage to be gained by the addition of a large portion of the total heat at or close to the top temperature of the cycle, has only at the present time been attained through the use of mercury. Substitutes that have been suggested are anhydrous aluminum bromide and zinc diamino chloride, both possessing practical difficulties. The writer feels that the solution and binary cycles require much greater and more thorough investigation before either can take their legitimate place in power-generation.

The Koenemann cycle has, however, two useful applications in the low-pressure low-temperature non-corrosive field. It can elevate low-pressure steam to a medium pressure by means of the addition of high-pressure steam, called combination, or it can elevate medium-pressure steam to a higher pressure.

This latter is called separation because the increased availability is obtained by rejecting a portion of the supply as exhaust steam.

Combination is an inexpensive method of increasing the availability of exhaust steam or increasing the steam pressure to permit the addition of several stages of evaporation to chemical manufacturing

processes. The addition of one high-pressure boiler and the use of a Koenemann transformer may be a substitute for adding a number of low-pressure boilers.

Separation also has an interesting practical application in the production of relatively high-pressure steam when medium-pressure steam is the only available source of heat. This is obtained as in

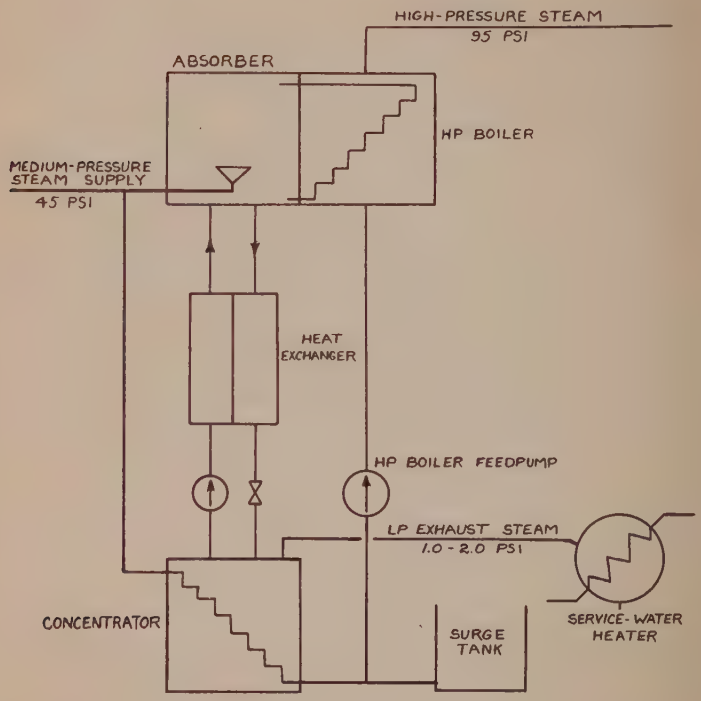

FIG. 1 KOENEMANN PROCESS FOR STEAM SEPARATION

Figure 1 by reversing the usual positions of the absorber and concentrator.

A comparison was made by the writer of the performance of a pressure transformer and an electrically-driven compressor for increasing district-heating steam pressure at 45 psi abs to 95 psi for use in certain laundry equipment operating at a high temperature

corresponding to the increased saturation pressure. The laundry considered in the writer's study was situated in an athletic-club building where it was not convenient to install a boiler plant with a twelve-to-fifteen-story chimney, and where the only source of steam was the district-heating main in the street. The compressor was installed as the most satisfactory means of raising the steam pressure. The study which considered the hypothetical operation of a Koenemann transformer in place of the compressor, showed that the transformer was economical only when part or all of the rejected low-pressure exhaust steam could be used for heating water for the laundry and club use. Based upon curves indicating the probable hourly variation during the day of the use of steam and hot water, and assuming that all low pressure exhaust steam could be utilized for water heating, the operation of the transformer showed a possible annual operating saving of 50.3 per cent exclusive of capital charges.

The possibilities of the Koenemann steam-pressure transformer appear to warrant additional chemical and metallurgical research.

R. L. HEINDEL, JR.: At the present time, do you have any idea of the limitation of the nature of solvents for such a cycle?

G. G. BROWN: I suppose you mean the temperature limitations?

R. L. HEINDEL, JR.: No, I was thinking more of the actual nature of the solvent. Were you referring only to aqueous solutions?

G. G. BROWN: No, there is no need of limiting the operation to aqueous solutions, or even to a single solution. It is rather difficult to use water in conjunction with caustic soda solution, or any other solute if water is to be the volatile component, at temperatures below thirty-five degrees Fahrenheit. It was suggested some years ago, by a Dr. Morris, that in refrigerating cycles we use a saline solution, sodium chloride, for the vaporizer to prevent the freezing of the water; but by duplexing an aqueous caustic solution for the high temperature end of the solution with an aqueous ammonia solution for the low temperature end of the cycle, heat can enter into the cycle at a high temperature depending upon the concentration of the caustic solutions used, and the useful purpose accomplished by ammonia as a volatile component for the low temperature range. The handling of the solutions is a chemical engineering problem.

Because we are using solutions instead of a single component, there is no reason why we cannot select any available material that suits our use, provided that it can be handled and operated without decomposition over the temperature range.

CHAIRMAN MARSHALL: If there are no further questions, we will proceed to the next paper on the program, "Studies in Agitation," which will be presented by Dr. A. McLaren White.

STUDIES IN AGITATION

By A. McLAREN WHITE,* EDWARD BRENNER,* G. A. PHILLIPS,* and M. S. MORRISON*

IV. Power Measurements

Despite the wide-spread and long-continued use of mixing and stirring machinery of all kinds, the design of equipment of this type still remains almost wholly empirical. Wood, Whittemore and Badger[5] in an early paper pointed out the surprising effectiveness of the simple paddle agitator. This result has been confirmed by other investigators.[1,2,4]

A method of predicting the power requirements of agitational equipment has long been needed. Wood, Whittemore and Badger[5] made preliminary power measurements during the course of their investigation of agitator performance. In this work, power was measured as input to the D.C. driving motor, less the power required to drive the shafting when the tank was empty. The results obtained were erratic, and admittedly rather inaccurate, as the shafting loss was usually greater than the power absorbed by the liquid. These results however indicate qualitatively that power demand increases rapidly with increase in rotational speed. More recently an excellent review of the literature has been given by Hixson and Wilkens[3] who report power measurement on several systems involving propeller agitators.

As part of a project designed to obtain a quantitative measure of stirrer performance, there have been made in this laboratory a large number of measurements of power consumption by simple paddle stirrers. In this work a steel tank 51 inches in diameter was used as a liquid container. This was subsequently equipped with false liners so that the diameter could be reduced to 41 inches and 30 inches respectively. The paddle was mounted horizontally on a vertical shaft driven through a ring-gear and pinion by a motor connected to a line shaft.

Preliminary efforts to measure power input by means of a watt-

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meter in the motor circuit proved unsatisfactory. Fluctuations of the watt-meter were often as large as the reading, and corrections for losses in shafts and gears proved difficult to obtain. It was evident that to attain any degree of accuracy it would be necessary to measure power absorbed at the agitator shaft, thus eliminating the dubious line loss corrections, and obtaining net power directly.

A torsion dynamometer was therefore constructed, as shown in Figure 1. The vertical agitator shaft was cut a short distance below

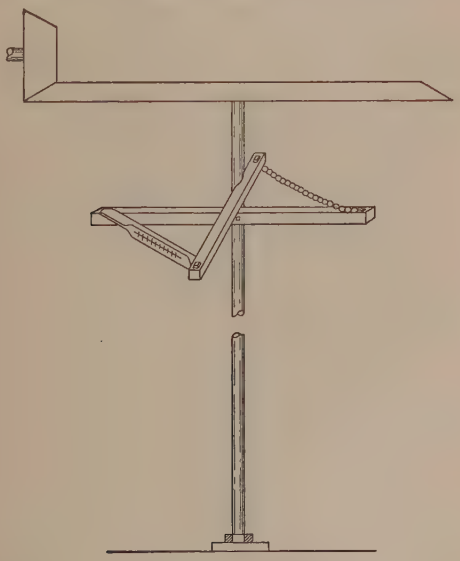

FIG. 1. Diagrammatic Representation of Large Dynamometer.

the ring gear and two iron bars, 1 inch square and 2 feet long, fastened one to each portion of the shaft. The bars were then connected at one end by a 100 pound spring scale, and at the other end by a safety chain. The dynamometer was calibrated by wedging the lower portion of the shaft, replacing the ring gear by a pulley of known diameter, and applying a known tangential load to the pulley by means of dead weights. The calibration was repeated at intervals during the work, and was found to remain substantially constant. As it proved difficult during a run to read directly the revolving spring scale, a sliding rider was constructed which could be pushed into

place against the pointer of the scale. On stopping the machine, the reading of the scale was obtained. The starting torque being much higher than that during the run, such readings were taken after the machine had reached a steady state. Scale readings were converted into torque by reference to the calibration curve, and agitator speeds were obtained by timing a given number of revolutions.

In Tables I, II, and III are reported results for tanks 51, 41, and 30 inches in diameter. Ten different paddles, ranging in length from 47 inches to 14 inches, and in width from 8 inches to 2 inches, were used. All paddles were of rough-sawed pine, rectangular in shape, and unbevelled. Paddles in all cases were approximately two and a quarter inches thick, and were placed in the tank so that their midpoints were 11¼ inches from the bottom of the tank, unless otherwise specified. In addition to water, Curbay Binder, obtained from the U. S. Industrial Alcohol Co., was diluted with varying amounts of water to study the effect of density and viscosity on the power requirements. Densities were measured by means of a hydrometer, and viscosities by means of a calibrated Saybolt Universal viscosimeter. In Tables I-III, columns 1 and 2 report paddle dimensions in inches, column 3 the substance stirred, columns 4, 5, and 6 the depth, absolute viscosity and density of the liquid studied, and columns 7 and 8 the agitator speed in revolutions per second, and the horsepower calculated from the observed torque and the speed.

To study the effect of certain variables not conveniently handled on the large machine, a smaller, and less sensitive, dynamometer was constructed as shown in Figure 2. In this machine torque was measured by observing the reaction of the containing vessel. Stirring was accomplished by means of a small water motor, the containing vessel being free to rotate. Weights were added to the pan in order to keep the container in zero position, and from this, with a knowledge of the dimensions of the container, torque was computed. Three different glass containers, with several different wooden paddles, were used as reported in Tables IV, V, and VI. In addition to water, glycerine, carbon tetrachloride, mineral oil, toluene, and sugar solution were studied. Various positions of the paddle with reference to the bottom of the container were also used.

TABLE I

Tank Diameter—51 inches

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
47	8	Water	2.0	0.000725	62.3	0.406	0.0316
						0.406	0.0296
						0.507	0.0635
						0.507	0.0596
						0.615	0.102
						0.615	0.0974
						0.750	0.212
						0.750	0.216
						0.900	0.347
						0.900	0.340
				0.000341	61.5	0.896	0.359
				0.000341	61.5		0.359
				0.000401	61.8		0.359
				0.000403	61.8		0.359
				0.000430	61.9		0.369
				0.000433	61.9		0.364
				0.000467	62.0		0.359
				0.000607	62.3		0.374
				0.000607	62.3		0.374
				0.000607	62.3		0.374
				0.000609	62.3		0.375
				0.000609	62.3		0.375
			2.5	0.000609	62.3	0.891	0.388
			2.5			0.891	0.388
			3.0			0.887	0.399
			3.0			0.887	0.399
			1.5			0.896	0.336
			1.5			0.896	0.338
47	6	Water	2.0	0.000725	62.3	0.583	0.0945
						0.917	0.317
						0.917	0.322
						0.750	0.173
						0.750	0.168
						0.517	0.0581
						0.517	0.0561
						0.667	0.126
		Curbay Binder		1.147	85.1	0.445	0.227
						0.447	0.230
						0.477	0.268
						0.481	0.268
		Curbay Binder plus water		0.191	82.6	0.543	0.220
						0.545	0.224
						0.482	0.159
						0.484	0.159
						0.650	0.352
						0.651	0.356
47	6	Curbay Binder, plus water	2.0	0.0769	81.0	0.678	0.313
						0.678	0.316
						0.735	0.385
						0.740	0.388

TABLE I—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
47	6	Curbay Binder, plus water	2.0	0.0769	81.0	0.568	0.197
						0.571	0.197
						0.490	0.129
						0.490	0.126
				0.0502	80.1	0.490	0.110
						0.491	0.110
						0.576	0.172
						0.575	0.173
						0.746	0.358
						0.755	0.363
						0.678	0.288
						0.680	0.282
				0.0363	78.9	0.687	0.268
						0.690	0.272
						0.775	0.376
						0.778	0.374
						0.580	0.160
						0.580	0.162
						0.490	0.101
						0.490	0.103
				0.0285	78.2	0.496	0.0981
						0.495	0.0981
						0.591	0.159
						0.591	0.156
						0.751	0.306
						0.726	0.290
						0.720	0.288
						0.699	0.264
						0.705	0.274
				0.00864	74.2	0.709	0.222
						0.709	0.222
						0.760	0.276
						0.757	0.270
						0.600	0.140
						0.599	0.142
						0.501	0.0878
						0.500	0.0876
				0.00409	71.7	0.502	0.0736
						0.502	0.0736
						0.607	0.132
						0.605	0.131
						0.766	0.260
						0.763	0.256
						0.721	0.218
						0.714	0.210
47	6	Curbay Binder, plus water	2.0	0.00239	69.5	0.716	0.198
						0.716	0.188
						0.716	0.192
						0.760	0.228
						0.754	0.227
						0.599	0.113
						0.597	0.111
						0.500	0.0671
						0.500	0.0714

TABLE I—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
47	4	Water	2.0	0.000753	62.3	0.759	0.133
						0.759	0.143
						0.615	0.0810
						0.615	0.0880
						0.910	0.228
						0.910	0.234
				0.000745		0.910	0.239
						0.770	0.151
						0.500	0.0562
						1.11	0.470
						1.11	0.476
47	2	Water	2.0	0.000745	62.3	1.10	0.312
						1.10	0.298
						0.908	0.191
						0.908	0.184
						0.606	0.0706
						0.606	0.0660
						0.740	0.120
						0.740	0.109
						0.500	0.0388
						0.500	0.0388
				0.000628	62.3	1.12	0.326
						1.12	0.329
						0.908	0.220
						0.908	0.220
						0.750	0.104
						0.750	0.110
						0.505	0.0368
						0.505	0.0368
						0.620	0.0627
						0.620	0.0650
			1.5	0.000616	62.2	0.910	0.168
			1.5			0.910	0.172
			2.0			0.897	0.188
			2.0			0.897	0.185
			2.5			0.903	0.204
			2.5			0.903	0.201
			3.0			0.903	0.226
			3.0			0.903	0.226
			3.5			0.903	0.218
			3.5			0.903	0.218
36	8	Water	2.0	0.000693	62.3	1.10	0.276
						1.10	0.276
						0.463	0.0280
						0.463	0.0301
						0.555	0.0336
						0.555	0.0336
						0.907	0.147
						0.907	0.147
						0.615	0.0480
						0.615	0.0480
						0.373	0.0128

TABLE I—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
36	8	Water	2.0	0.000693	62.3	0.373	0.0128
						0.504	0.0261
						0.504	0.0261
						0.744	0.0810
						0.744	0.0810
		Curbay Binder	2.0	1.147	85.1	0.529	0.209
						0.531	0.207
						0.481	0.158
						0.480	0.160
						0.669	0.347
						0.667	0.346
						0.720	0.405
						0.720	0.408
36	6	Water	2.0	0.000693	62.3	0.620	0.0481
						0.620	0.0481
						0.920	0.168
						0.920	0.174
						0.755	0.0944
						0.755	0.0944
						0.506	0.0307
						0.506	0.0307
						0.610	0.0520
						0.610	0.0497
						1.10	0.239
						1.10	0.242
				0.000634	62.3	0.907	0.143
						0.907	0.145
						0.750	0.0909
						0.750	0.0930
						0.505	0.0260
						0.505	0.0260
						0.615	0.0450
						0.615	0.0476
						1.11	0.264
						1.11	0.271
36	4	Water	2.0	0.000672	62.3	0.744	0.0690
						0.744	0.0718
						0.910	0.113
						0.910	0.113
						0.610	0.0369
						0.610	0.0369
				0.000693	62.3	0.500	0.0259
						0.500	0.0281
						1.11	0.206
						1.11	0.205
25	6	Water	2.0	0.000637	62.3	0.610	0.0160
						0.610	0.0160
						0.748	0.0257
						0.748	0.0257
						0.911	0.0432

TABLE I—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
25	6	Water	2.0	0.000637	62.3	0.911	0.0432
						1.11	0.0770
						1.11	0.0815
24	8	Water	2.0	0.000644	62.3	0.930	0.0399
						0.930	0.0399
						0.755	0.0228
						0.755	0.0228
						0.620	0.0130
						0.620	0.0115
						0.605	0.0158
						0.605	0.0158
						0.870	0.0423
						0.870	0.0423
						1.10	0.0642
						1.10	0.0662
		Curbay Binder	2.0	1.147	85.1	1.05	0.343
						1.03	0.340
						0.880	0.218
						0.878	0.219
						0.739	0.139
						0.739	0.134
						0.506	0.0550
						0.507	0.0570
						0.615	0.0880
						0.615	0.0855
14	8	Curbay Binder	2.0	1.147	85.1	0.508	0.0102
						0.508	0.00919
						0.617	0.0186
						0.620	0.0199
						0.914	0.0474
						0.914	0.0474
						0.754	0.0258
						0.750	0.0273
						1.12	0.0776
						1.12	0.0776

TABLE II

Tank Diameter—41 inches

36	8	Water	2.0	0.000658	62.3	1.10	0.272
						1.10	0.274
						0.745	0.0867
						0.745	0.0867
						0.908	0.140
						0.908	0.148
						0.610	0.0446
						0.610	0.0446
						0.503	0.0238
						0.503	0.0238

TABLE II—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
36	6	Water	2.0	0.000634	62.2	1.11	0.250
						1.12	0.256
						0.901	0.132
						0.901	0.135
						0.740	0.0747
						0.740	0.0747
						0.505	0.0261
						0.505	0.0239
						0.615	0.0425
						0.615	0.0425
36	4	Water	2.0	0.000655	62.3	0.610	0.0344
						0.610	0.0370
						0.500	0.0181
						0.500	0.0192
						0.740	0.0603
						0.740	0.0603
						0.900	0.107
						0.900	0.112
						1.10	0.193
						1.10	0.196
25	6	Water	2.0	0.000633	62.2	0.620	0.0130
						0.620	0.0130
						0.753	0.0228
						0.753	0.0260
						0.925	0.0486
						0.925	0.0486
						1.11	0.0769
						1.11	0.0768
24	8	Water	2.0	0.000634	62.2	1.12	0.0771
						1.12	0.0724
						0.907	0.0390
						0.907	0.0409
						0.745	0.0256
						0.751	0.0258
						0.605	0.0130
						0.605	0.0130
						0.620	0.0172
						0.613	0.0185

TABLE III

Tank Diameter—30 inches

25	6	Water	2.0	0.000622	62.2	1.11	0.0628
						1.11	0.0674
						0.911	0.0391
						0.911	0.0391
						0.748	0.0196
						0.748	0.0224
						0.610	0.0128
						0.610	0.0128

TABLE III—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
24	8	Water	2.0	0.000618	62.2	0.610	0.0128
						0.506	0.00580
						0.787	0.0238
						0.784	0.0237
						0.935	0.0400
						0.910	0.0349
				0.000628	62.2	1.12	0.0674
						1.12	0.0674

TABLE IV

Tank Diameter—7.0625 inches

6.6	1.11	Water	0.277	0.000562	62.2	1.57	0.000086
						2.88	0.000747
						2.38	0.000357
						1.72	0.000148
						2.36	0.000370
						2.73	0.000578
						2.98	0.000774
						2.03	0.000208
						1.75	0.000137
						1.54	0.000097
			0.198	0.000534		2.84	0.000621
						1.71	0.000108
						1.91	0.000196
						2.60	0.000428
						2.79	0.000572
						3.11	0.000776
						0.91	0.000021
						1.93	0.000167
						2.70	0.000510
						2.00	0.000188
				0.000604		2.58	0.000435
						2.56	0.000503
						1.77	0.000139
						2.28	0.000251
						2.68	0.000444
						1.72	0.000121
						2.51	0.000416
						2.94	0.000602
		Glycerine	0.167	0.107	77.0	0.63	0.000074
						1.20	0.000208
						0.20	0.000032
						0.90	0.000170
						0.76	0.000090
						1.01	0.000222
						0.49	0.000043
						0.88	0.000145
						1.03	0.000202
						0.87	0.000130

TABLE IV—*Continued*

Paddle Length (inches)	Paddle Width (inches)	Liquid Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
6.6		CCl_4	0.198	0.000579	99.0	1.01	0.000040
						1.87	0.000278
						2.34	0.000496
						1.38	0.000108
						1.92	0.000270
						2.40	0.000509
						0.82	0.000013
						1.68	0.000172
						2.25	0.000425
6.6	1.11	Mineral Oil	0.198	0.012850	52.1	0.65	0.000031
						1.28	0.000141
						1.59	0.000225
						1.88	0.000369
						1.98	0.000416
						1.13	0.000089
						1.68	0.000277
						2.03	0.000461
		Radiator Glycerine		0.00530	68.7	1.83	0.000359
						1.42	0.000156
						1.12	0.000088
						1.39	0.000175
						1.68	0.000290
						1.96	0.000446
						2.11	0.000496
						1.34	0.000169
						0.87	0.000048
		Toluene		0.000369	53.6	3.03	0.000666
						2.41	0.000246
						2.72	0.000404
						1.75	0.000069
						2.50	0.000294
						2.78	0.000414
						3.08	0.000630
						2.23	0.000210
		Sugar Sol'n. (Approx. 50%)		0.007620	76.2	0.93	0.000051
						1.87	0.000382
						1.72	0.000310
						1.21	0.000104
						1.78	0.000308
						1.41	0.000166
						1.88	0.000392
						2.08	0.000490
						1.40	0.000143
		Lub. Oil		0.013280	52.8	1.61	0.000278
						1.92	0.000451
						1.22	0.000134
						1.39	0.000186
						1.83	0.000384
						1.55	0.000243
						1.80	0.000353
						0.83	0.000052

TABLE IV—*Continued*

Paddle Length (inches)	Paddle Width	Liquid Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
5.5	3.44	Water	0.541	0.000561	62.2	1.51	0.000083
						1.95	0.000183
						2.35	0.000332
						2.53	0.000415
						2.66	0.000520
						2.12	0.000232
						1.62	0.000114
						1.40	0.000066
						1.90	0.000164
						2.18	0.000256
5.5	2.187	Water	0.541	0.000571	62.3	1.77	0.000124
						2.40	0.000300
						2.97	0.000580
						2.32	0.000274
						2.92	0.000573
						2.63	0.000409
						2.06	0.000194
						1.72	0.000107
						1.40	0.000055
	1.125			0.000576	62.3	1.67	0.000091
						2.02	0.000172
						2.75	0.000430
						2.61	0.000307
						3.04	0.000572
						2.22	0.000226
						1.90	0.000149
						1.26	0.000049
4.63	1.110		0.198	0.000597	62.3	3.63	0.000398
						2.43	0.000133
						3.04	0.000311
						3.06	0.000360
						2.46	0.000155
						2.70	0.000212
						3.00	0.000282
						2.30	0.000108
						2.75	0.000194
						3.50	0.000411
						2.35	0.000129
						3.22	0.000329
						2.60	0.000123
						3.15	0.000260
				0.000610	62.3	1.85	0.000043
						2.81	0.000154
						3.62	0.000338
						3.35	0.000262
						2.54	0.000119
						3.49	0.000327
						3.45	0.000310
			0.416			2.12	0.000100
						3.37	0.000408
						3.82	0.000596
						4.38	0.000924

TABLE IV—*Continued*

Paddle Length (inches)	Paddle Width	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
4.63	1.110	Water	0.416	0.000610	62.3	4.35	0.000845
						3.78	0.000589
						3.17	0.000349
						2.76	0.000228
						2.28	0.000143
4.63	1.110	Water	0.585	0.000612	62.3	2.54	0.000208
						3.30	0.000440
						3.57	0.000557
						4.22	0.000960
						4.03	0.000823
						3.62	0.000594
						3.03	0.000356
						2.60	0.000234
						2.06	0.000129
			Paddle Height Variable				
			Paddle Height—4.44 inches				
4.63	1.110	Water	0.585	0.000602	62.2	2.96	0.000300
						3.29	0.000414
						1.67	0.000065
						2.02	0.000133
						2.47	0.000193
						3.21	0.000378
						3.47	0.000516
						1.75	0.000069
			Paddle Height—6.00 inches				
						2.55	0.000240
						3.06	0.000337
						2.31	0.000163
						1.66	0.000091
						1.67	0.000654
						2.62	0.000266
				0.000595	62.2	2.50	0.000216
						3.30	0.000413
						3.64	0.000569
						2.28	0.000160
						1.76	0.000083
						2.18	0.000153
						2.93	0.000322
						3.57	0.000558
						3.00	0.000375
			Paddle Height—4.25 inches				
				0.000596	62.2	2.19	0.000137
						3.02	0.000354
						3.37	0.000502
						2.93	0.000344
						2.08	0.000147
						1.85	0.000087
			Paddle Height—1.94 inches				
4.63	1.110	Water	0.585	0.000595	62.2	3.63	0.000600
						2.66	0.000209
						3.08	0.000360
						2.88	0.000294
						3.50	0.000171

TABLE IV—*Continued*

Paddle Height—0.75 inches

Paddle Length (inches)	Paddle Width (inches)	Substance	Liquid Depth (feet)	Liquid Absolute Viscosity (lb./sec.-ft.)	Liquid Density (lb./cu.ft.)	Agitator Speed (R.P.S.)	Agitator H.P.
4.63	1.110	Water	0.198	0.000637	62.3	2.82	0.000143
						4.08	0.000464
						3.61	0.000340
						2.79	0.000153
						3.48	0.000300
						4.38	0.000510
						3.14	0.000222
						2.44	0.000095

TABLE V

Tank Diameter—5.0 inches

4.63	1.110	Water	0.198	0.000597	62.3	1.52	0.000024
						2.00	0.000053
						3.68	0.000290
						3.36	0.000195
						4.20	0.000376
						3.58	0.000320
						3.41	0.000216
						3.69	0.000392
				0.000586		2.15	0.000069
						4.53	0.000631
						4.23	0.000541
						3.81	0.000396
						3.44	0.000276
						2.93	0.000172
						2.86	0.000153
						3.60	0.000288
						4.50	0.000626
						1.22	0.000026

TABLE VI

Tank Diameter—6.0 inches

4.63	1.110	Water	0.198	0.000553	62.1	2.50	0.000081
						4.55	0.000527
						3.29	0.000232
						4.16	0.000680
						3.75	0.000338
						3.20	0.000206
						2.43	0.000079
						2.97	0.000153
						4.00	0.000488
						2.50	0.000145
				0.000586		3.08	0.000198
						4.32	0.000502
						4.51	0.000580
						2.47	0.000080
						3.80	0.000318
						4.24	0.000465
						3.93	0.000378
						3.18	0.000204
						2.92	0.000151
						2.35	0.000091

While results on the large dynamometer could be checked with considerable accuracy, those on the small dynamometer are less consistent. An average curve can, however, be drawn through these points with satisfactory results.

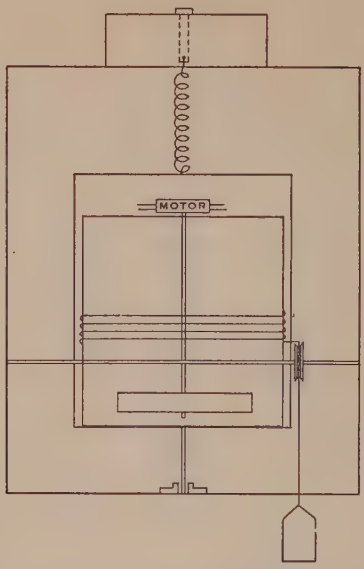

Fig. 2. Diagrammatic Representation of Small Dynamometer.

Acknowledgment

We are indebted to the U. S. Industrial Alcohol Co., for kindly donating the Curbay Binder used in these experiments.

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STUDIES IN AGITATION

By A. McLAREN WHITE and EDWARD BRENNER
University of North Carolina

V. The Correlation of Power Data

The data on power consumption by paddle agitators reported in the preceding paper are of interest chiefly as material for a possible generalization expressing power demand in terms of the significant variables. The present paper presents such a correlation.

It seems logical to expect that the power consumption of a simple paddle agitator will depend on the following variables: paddle length and width, tank diameter, liquid depth, agitator speed, and on the physical properties of the fluid stirred. Roughness undoubtedly plays an important part, but inasmuch as this factor is incapable of numerical evaluation it will be omitted for the present. As will be shown later, paddle thickness and the position of the paddle with relation to the bottom of the tank seem to have negligible influence on power consumption.

From a consideration of the dimensions of the above variables, it is possible to derive a dimensional equation relating power with other variables. In exponential form, this equation may be written:

$$\frac{P}{\rho N^3 L^5} = K \left(\frac{z}{L^2 N \rho}\right)^a \left(\frac{W}{L}\right)^b \left(\frac{H}{L}\right)^c \left(\frac{D}{L}\right)^d \qquad (1)$$

where z absolute viscosity
L paddle length
N agitator speed
W paddle width
D tank diameter
H liquid depth
ρ liquid density
K, a, b, c, d constants to be determined experimentally
P power absorbed by the stirrer

Using the data of White, Brenner, Phillips, and Morrison, previously presented, the values of the unknown constants have been determined for the region of turbulent flow.

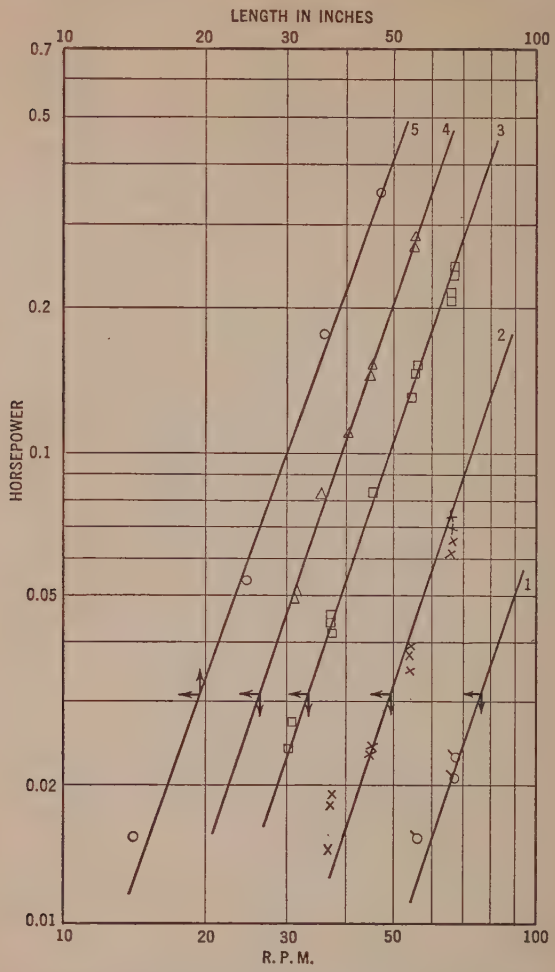

FIG. 1. Effect of length and rotational speed for paddle width 0.5 feet. Curves 1-4 show power versus speed for lengths 14, 25, 36 and 47 inches. Curve 5 indicates power versus length at 60 R.P.M.

Plots of agitator speed versus power consumption were drawn on a log-log paper for a number of runs with both large and small dynamometers. Straight lines resulted as shown in Figure 1. The

slopes of these lines, while varying slightly from run to run, deviated very little from an average value of 2.9. Since, during a run, all other conditions remained constant, it follows that power varies as the 2.9 power of the rotational speed. Referring to Equation 1, it is seen that N, the agitator speed, occurs in two dimensionless groups, whence, all other factors remaining constant,

$$\frac{P}{N^3} = K' \left(\frac{1}{N}\right)^a \qquad (2)$$

From this the exponent a must have the value 0.1, if the dimensional analysis has been properly carried out.

To determine the effect of paddle length, log-log plots were made of power versus speed for various paddle lengths, all other factors being held constant. Interpolating at constant agitator speed, curves of power versus paddle length were constructed as shown in Figure 1. These curves for various paddle widths, while slightly irregular, were essentially straight lines of average slope 2.8 when plotted on log-log paper. From this, all other factors being constant, power consumption varies as the 2.8 power of the paddle length. Referring to Equations 1 and 2, the holding all other variables constant,

$$\frac{P}{L^5} = K''\left(\frac{1}{L^2}\right)^{0.1}\left(\frac{1}{L}\right)^b\left(\frac{1}{L}\right)^c\left(\frac{1}{L}\right)^d \qquad (3)$$

From the above, it therefore follows that the sum of the values of the exponents b, c, and d must equal 2.0.

Data for various widths of paddles were then plotted as shown in Figure 2. Interpolating at constant speed, all other factors remaining constant, log-log plots of power versus paddle width were made. These proved to be straight lines of average slope 0.3, indicating that power varies as the 0.3 power of paddle width. The exponent b in Equation 1 was therefore assigned the value 0.3.

The effect of liquid depth was more difficult to determine. Owing to the construction of the large dynamometer, it was impossible to vary the depth of the fluid over a wide enough range to obtain satisfactory results. Recourse was therefore had to the less accurate small dynamometer, in which liquid depth could be varied over an appreciable range. Figure 3 shows a plot of power versus liquid depth, other factors remaining constant. A consideration of these

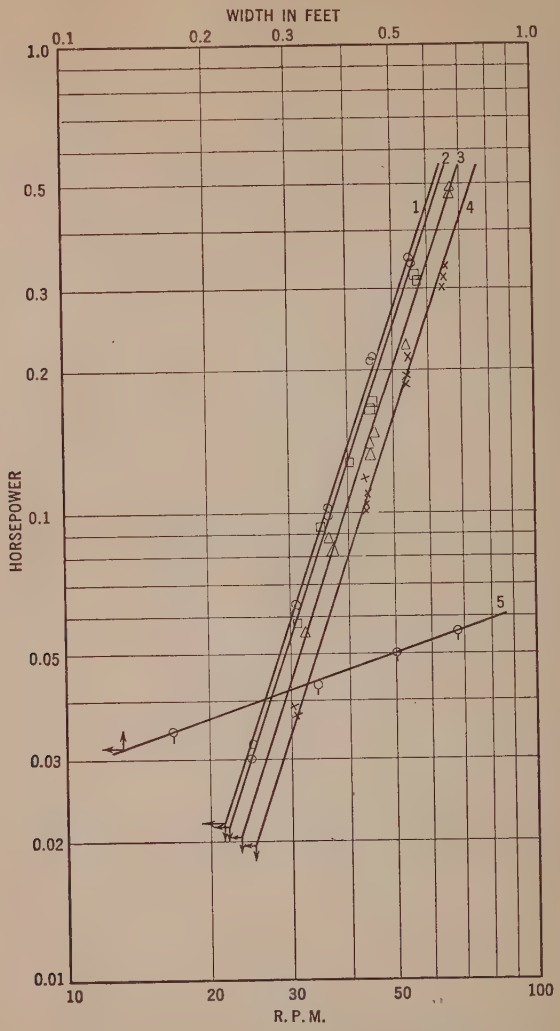

FIG. 2. Effect of paddle width for paddles 47 inches long. Curves 1-4 show power versus rotational speed for widths 0.667, 0.500, 0.333 and 0.167 feet. Curve 5 shows power versus width at 30 R.P.M.

data, together with those of the large dynamometer, leads us to recommend a value of 0.6 for the exponent c in Equation 1. While the available evidence is not regarded as conclusive, the recommended

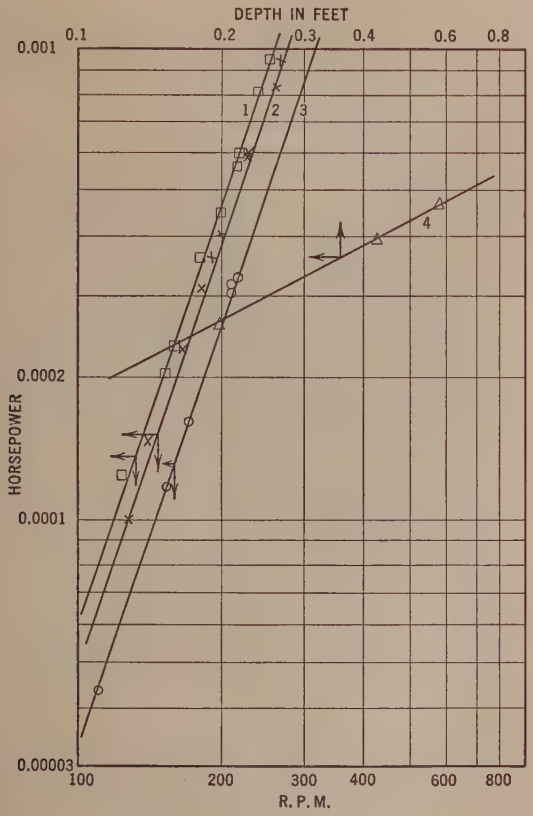

FIG. 3. Effect of liquid depth for paddle 4.63 x 1.11 inches. Curves 1-3 show power versus rotational speed for water depths 0.589, 0.416 and 0.198 feet. Curve 4 shows power versus depth at 200 R.P.M.

value for this exponent is considered sufficiently reliable to be used for purposes of estimate.

The effect of tank diameter is not well established. In Figure 4 are plotted results with both large and small dynamometers. Reading

from the power-speed curves at constant speed, and plotting against tank diameter gives curves roughly parabolic in shape. From this it would appear that power is not a simple exponential function of container diameter. The experimental evidence available, however,

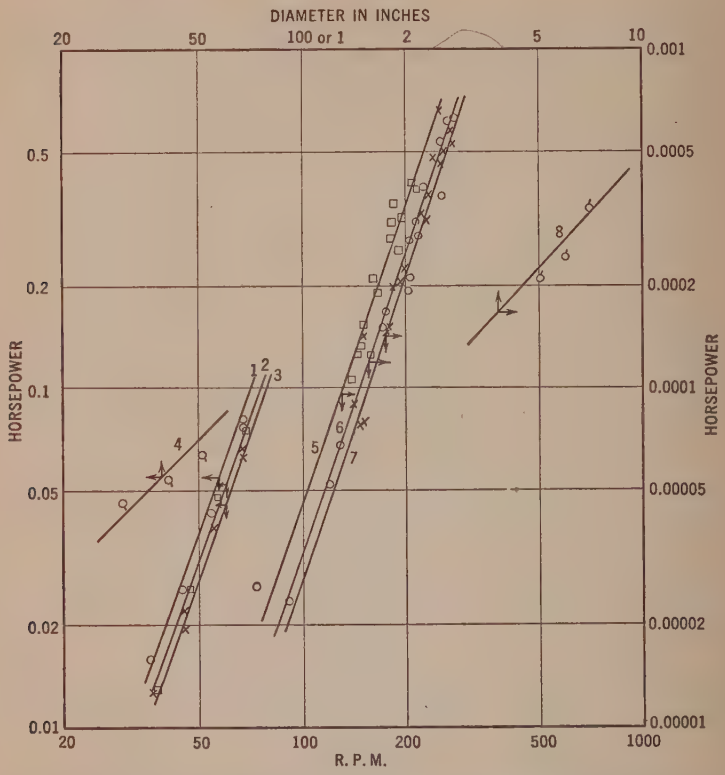

FIG. 4. Effect of tank diameter. Curves 1-3 from large dynamometer, curves 5-7 from small dynamometer, showing power versus rotational speed. Curves 4 and 8, for large and small dynamometers respectively, show power versus tank diameter.

is not sufficient to determine the form of this function. Efforts to relate power to the clearance of the paddle tip have so far proved unsuccessful. A consideration of the exponents previously determined shows that to satisfy Equation 1, the exponent d must have the value 1.1 Through the power-diameter points of Figure 4 have been

drawn straight lines of slope 1.1. While these lines cannot be considered as good representations of the data, they at least approximate the experimental points. We therefore suggest the use of the value 1.1 for exponent d until such time as more satisfactory and conclusive experimental evidence is available.

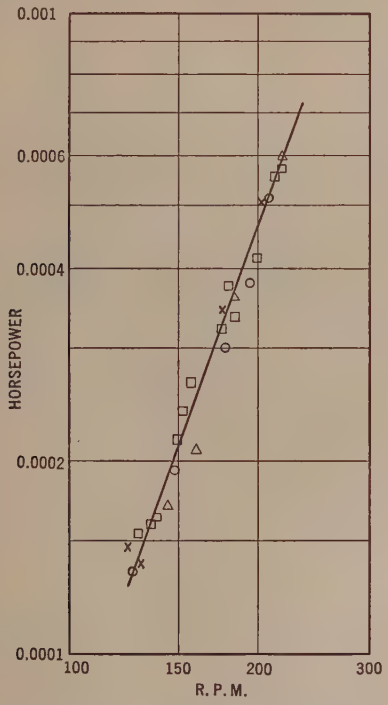

FIG. 5. Effect of paddle height, for paddle 4.63 x 1.11 inches. Liquid depth 7.06 inches. Distance from bottom of paddle to bottom of tank: □ 0.50, O 0.37, X 0.35, and △ 0.16 feet.

The distance of the paddle from the bottom of the container apparently has negligible effect on the power consumption of the stirrer. Figure 5 shows experimental points obtained with the small dynamometer for four different liquid depths. These data superimpose to such an extent that the drawing of individual lines through each set is unwarranted. Unpublished data on the large dynamometer

confirm the conclusion that for practical purposes the effect of paddle height may be neglected.

Paddle thickness seems to have little influence on the power consumption of an agitator. The data obtained in a series of unpublished tests on each dynamometer indicate that power is substantially independent of blade thickness, even with a four-fold increase in thickness.

Roughness undoubtedly plays an important role in power consumption, as has frequently been pointed out.[2] While roughness should enter a dimensional equation in the units of length, at present no numerical scale of roughness is available. The data here under discussion were obtained, in the case of the large dynamometer, using a painted steel tank, and unpainted rough-sawed wooden paddles. In the small dynamometer, glass vessels and dressed paddles were used. A smooth finish on the paddles in the former case would probably reduce power consumption, but the finish chosen seems fairly representative of current industrial practice.

The form of Equation 1 suggests that experimental results be plotted as two dimensionless groups, one a modified Reynolds number $\frac{L^2N\rho}{z}$, and the other containing the remaining terms of the expression. Substituting in Equation 1 the determined values for exponents *b*, *c*, and *d*, this second group becomes

$$\frac{P}{L^3N^3\rho D^{1.1}W^{0.3}H^{0.6}}$$

However calculation is simplified slightly if for the terms $L^2N\rho$ in the denominator are substituted their dimensional equivalent *z*. This is justifiable mathematically since the expression is to be plotted against the modified Reynolds number, and the terms interchanged occur respectively in numerator and denominator of the Reynolds number. The two methods of plotting will result in lines of different slope. Equation 2 indicates that the former method should yield a line of slope —0.1, while the latter should give a slope of 0.9, for the turbulent regime.

In Figure 6 are plotted the experimental data obtained with the large dynamometer. The group

$$\frac{P}{LzN^2D^{1.1}W^{0.3}H^{0.6}}$$

is here plotted against the modified Reynolds number, the term P being expressed in horse-power. The data at high Reynolds numbers give a straight line of slope 0.9 as predicted above, indicated by the broken curve in the figure. At low Reynolds numbers there is a change in slope.

Figure 7 is a similar plot for the data obtained with the small

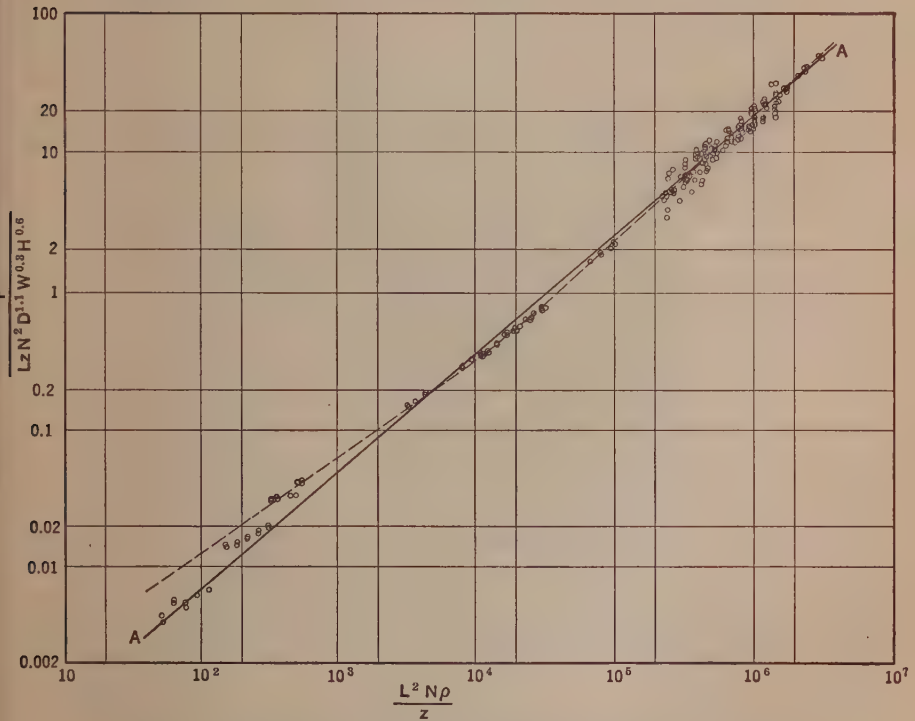

FIG. 6. Correlation of data from large dynamometer. Broken line is recommended curve solid line that of equation 5.

dynamometer. These, being obtained with a less sensitive instrument, are, as would be expected, more erratic. They confirm, however, the results obtained with the large machine. On this plot are also shown the data of Hixson and Wilkens [2] who measured the power absorbed by a four-bladed propeller in a tank with and without baffles. These experimenters painted all equipment with Bakelite

varnish, and were therefore dealing with smoother surfaces than in the work on which this discussion is based. In addition the effect of multiple blades and of propeller pitch is introduced. Their data on unbaffled stirring fall considerably below the data of the present work, while their results on baffled agitation are practically coincident

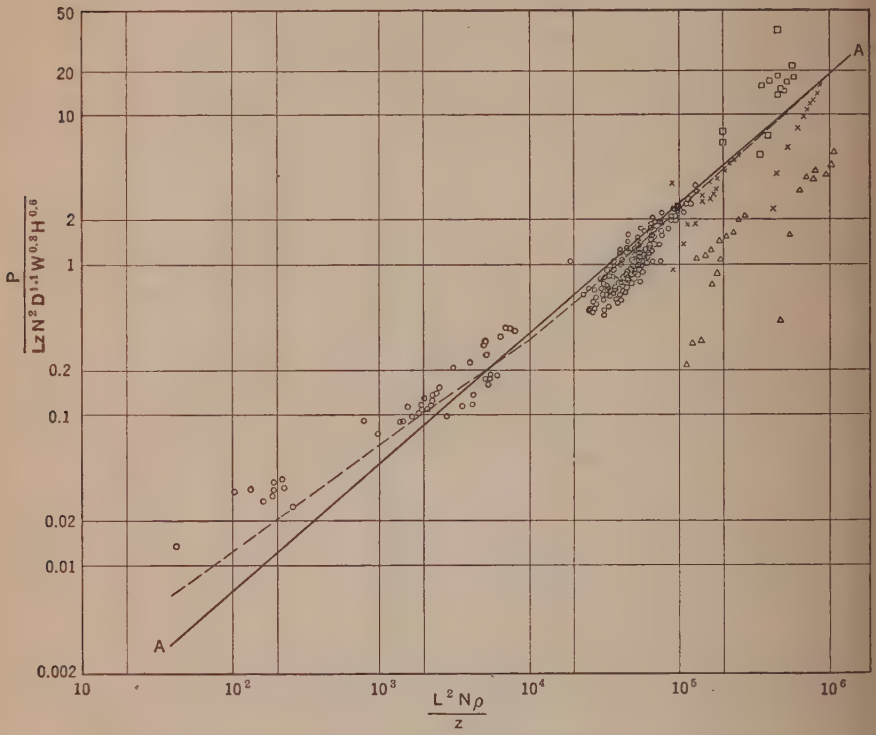

FIG. 7. Correlation of data from small dynamometer, and of other investigators. Broken line is recommended curve, solid line that of equation 5.

O Present work.
△ Hixson and Wilkens (unbaffled).
× Hixson and Wilkens (baffled).
□ Wood and Whittemore.

with the recommended curve. The discrepancy between the curve of Figure 7 and that for unbaffled propeller agitation may be due in part to differences in roughness and in part to difference in design of the agitator.

Figure 7 also includes unpublished data of Wood and Whittemore, included through the courtesy of Professor W. L. Badger who kindly permitted the examination of their original records. These data were obtained with the apparatus described by Wood, Whittemore and Badger.[3] The agitator blade was of the two-bladed propeller type 50 inches long and 3.4 inches wide, and was contained in a tapering wood-stave tank of average diameter 56 inches. These results, although rather erratic due to the difficulty in correcting for shafting losses, confirm in general the present work. The roughness in this case was undoubtedly greater than in the other work here considered, for the paddle blade was badly worn and the inside surface of the tank somewhat shredded. This seems to account, at least in part, for the greater power consumption.

From a consideration of the data presented in Figures 6 and 7 it appears that, while there is no marked critical velocity, there is a change in slope at a Reynolds number of about 20,000. This indicates that the exponents in Equation 1 are not constant over the entire range, and that the form of the function is best expressed graphically. The broken curve shown in these figures is recommended as most representative of the present data, due weight being given to the results obtained with each dynamometer. The solid line A-A shown in these figures fits the data a little less well, but is capable of more direct mathematical expression. The equation for this line, power being given as horse-power, is

$$\frac{P}{LzN^2D^{1.1}W^{0.3}H^{0.6}} = 0.000129 \left(\frac{L^2N\rho}{z}\right)^{0.86} \qquad (4)$$

whence,

$$P = 0.000129\, L^{2.72}z^{0.14}N^{2.86}\rho^{0.86}D^{1.1}W^{0.3}H^{0.6} \qquad (5)$$

where N = revolutions per second, L = absolute viscosity (lbs. per sec.-ft.), ρ = lbs. per cu. ft., and all length terms are in feet. This equation expresses the experimental data satisfactorily for Reynolds number of 10,000 or more, but diverges at lower values.

The transition from turbulent to viscous flow apparently takes place gradually between Reynolds numbers of 2,000 and 20,000. This is in accord with evidence obtained with turbine wheels, in which

case no definite critical velocity is obtained.[2] The slope of the lower portion of the broken curve of Figures 6 and 7 is 0.70.

Buckingham [1] in a study of the windage of turbine wheels, concludes that power can best be expressed by the equation

$$P = C\rho^{0.9}N^{2.9}L^{4.8}z^{0.1} \qquad (6)$$

The exponents of density, viscosity, and rotational speed are identical with those of the upper part of the broken curve of Figures 6 and 7. As turbine wheel diameter was the only length variable considered by Buckingham, his exponent for the term L varies from that given here by an amount equal to the sum of the exponents of the other length variables introduced.

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2. Hixson and Wilkens, Ind. Eng. Chem., **25**, 1196 (1930).
3. Wood, Whittemore and Badger, Chem. Met. Eng., **27**, 1176 (1922).

Discussion

Chairman Marshall: This very practical paper, prepared by Dr. White and associates from the University of North Carolina, is open for discussion.

C. C. Furnas: Is there any indication that the relation between power and the diameter there is cyclic?

A. McL. White: We have not been able to get it that way, but it looks as though it ought to be. That is, our explanation of that minimum is that there is a natural vortex, or perhaps a standing wave, formed at that velocity. I was thinking of making a large tank to see if we could get a second minimum.

O. Racines (student member): I should like to ask how do you determine the extent of agitation? For instance, you have the small tank and the large tank. How do you know you have reached the same point of efficiency in agitating whatever you have within the tank?

A. McL. White: That is the problem we are trying to solve. We are attempting to attack the problem from another angle at the same

time, measuring the activity of the agitator by means of suspension of sand. That work is not ready for reporting at the present time.

CHAIRMAN MARSHALL: Is there any further discussion? (None.) We have on the program two papers which will be read by title: "Temperature-Time Relations Resulting from the Electrical Heating of the Face of a Slab," by Albert B. Newman; and "Chemical Engineering Laboratory Demonstrations—Some New Developments," by Charles R. Johnson.

THE TEMPERATURE-TIME RELATIONS RESULTING FROM THE ELECTRICAL HEATING OF THE FACE OF A SLAB

By ALBERT B. NEWMAN *

In the literature are many solutions of the heat diffusion equation for cases of slabs being heated or cooled, with boundary conditions involving the maintaining of a constant temperature either at the face or in the heating or cooling medium. The mathematical treatment of cases involving a controlled heat input rate may be said to have originated with Lord Kelvin in his concept of "heat sources" but the literature contains little information about the application of this concept to tangible cases. It is the purpose of this paper to present a theoretical analysis of the temperature-time relations resulting from three different cases of controlled heat input rates, and to reduce the results to a form usable by designers. The final objective of the paper is to present tables and curves for cases of slab heating in which it is required to heat to a desired temperature at the center without heating the face above a permissible maximum. The vulcanizing of rubber is an example, and there are many other possible applications.

Nomenclature

K = thermal conductivity in $\frac{\text{B.T.U. ft.}}{\text{ft.}^2\ \text{hr.}\ ^\circ\text{F}}$

C = specific heat in $\frac{\text{B.T.U.}}{\text{lb.}\ ^\circ\text{F}}$

ρ = density in $\frac{\text{lb.}}{\text{ft.}^3}$

$k = \frac{K}{C\rho}$ = thermal diffusivity in $\frac{\text{ft.}^2}{\text{hr.}}$

* Professor of Chemical Engineering, Cooper Union, New York, N. Y.

θ = time in hours from the beginning of heating period.

θ_1 = value of θ at end of heating period, in hours.

q = variable rate of heat input in $\frac{\text{B.T.U.}}{\text{ft.}^2\,\text{hr.}}$

q_o, q_1, q_m = respectively: initial, final, mean, rate of heat input in $\frac{\text{B.T.U.}}{\text{ft.}^2\,\text{hr.}}$

b = rate of increase or decrease of heating rate in $\frac{\text{B.T.U.}}{\text{ft.}^2\,\text{hr.}^2}$

t = temperature in degrees F, varying with x and θ.

x = distance in the direction of heat flow, measured from the center, in feet.

$P = \frac{\pi^2 k\theta}{a^2}$ = a dimensionless ratio; $P_1 = \frac{\pi^2 k\theta_1}{a^2}$

a = the half-thickness of the slab, in feet.

The M-function of x/a and P:

$$M(x/a; P) = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{-(-1)^n}{n^2} e^{-n^2 P} \cos(n\pi x/a).$$

The N-function of x/a and P:

$$N(x/a; P) = \frac{2}{\pi^4} \sum_{n=1}^{\infty} \frac{-(-1)^n}{n^4} e^{-n^2 P} \cos(n\pi x/a).$$

$B = \frac{K}{q_m a}$ = an abbreviation.

General Conditions of the Problem

It is assumed that heat is being actually driven into the face of the slab at the rate specified in each case, no allowance being made for the heat capacity of the heating element, for heat leakage from the other side of the heating element or for surface resistance between the heating element and the face of the slab; all of these factors must be allowed for in actual design. It is specified that the slab of thickness 2a is being heated at its two faces ($x/a = \pm 1$), or that a slab of thickness a is heated at one face ($x/a = 1$) and perfectly heat-insulated at the other ($x/a = 0$); the solution is identical for the two cases, and the derivations are based on the latter. Solutions are given for three types of heating rates, and for each type of heating rate there are two equations representing the temperature-time relations, one covering the heating period and the other the period after the heating is discontinued (the equalizing period). During the equalizing period it is assumed that no heat leaves or enters the slab at either face.

Case I. Heating Period Linearly Increasing Heating Rate

At the start ($\theta = 0$), the slab has the uniform temperature t_o and the heating rate is 0. The heating rate at the face $x/a = 1$ is increased linearly with time, or $q = b\theta$. Heating is abruptly discontinued at $\theta = \theta_1$, when $q_1 = b\theta_1$. The equation must satisfy all of the following five conditions:

$$\text{(a)}\ \frac{\partial t}{\partial \theta} = k\frac{\partial^2 t}{\partial x^2};\ \text{(b)}\frac{\partial t}{\partial x} = 0 \text{ at } x = 0;$$

$$\text{(c)}\frac{\partial t}{\partial x} = \frac{q}{K} = \frac{b\theta}{K} \text{ at } x/a = 1;\ \text{(d)}\ t - t_o = 0 \text{ when } \theta = 0;$$

and the total heat content at any time must equal the heat which has been put in up to that time, or

$$\text{(e)}\quad \int_0^a (t - t_o)C\rho dx = \int_0^\theta b\theta d\theta = \frac{b\theta^2}{2}.$$

It is also to be noted that $2q_m = q_1$.

An equation, in dimensionless form, which satisfies all of these conditions is:

$$B(t-t_o) = \frac{P}{P_1}\left\{\frac{P}{\pi^2} - \frac{1}{3} + \left(\frac{x}{a}\right)^2 + \frac{2\pi^2}{P}\left[\frac{1}{24}\left(\frac{x}{a}\right)^4 - \frac{1}{12}\left(\frac{x}{a}\right)^2 + \frac{1}{24} - \frac{1}{45} - N(x/a;P)\right]\right\} \quad (1)$$

By substituting the values of the symbols given in the table of nomenclature and performing the partial differentiations and integrations indicated in the five conditions which must be met, it may readily be proved that equation (1) does comply with all of these conditions, provided it be known that

$$N(x/a;0) = \frac{2}{\pi^4}\sum_{n=1}^{\infty}\frac{-(-1)^n}{n^4}\cos(n\pi x/a) = \frac{x^4 - 2a^2x^2 + a^4}{24a^4} - \frac{1}{45} \quad (2)$$

Equation (2) gives the value of $N(x/a;P)$ when $P = 0$.

Case I. Temperature Equalizing Period

If no heat is allowed to escape from the heated face ($x/a = 1$) after heating is discontinued, θ being measured from the beginning of the heating period, the time-temperature relations from then on will be represented by:

$$B(t-t_o) = \frac{P_1}{\pi^2} - 2M(x/a; P-P_1)$$

$$- \frac{2\pi^2}{P_1}\left[N(x/a; P) - N(x/a; P-P_1) \right] \qquad (3)$$

Equation (3) must reduce to equation (1) when $\theta = \theta_1$, and this can be shown to be true by means of equations (2) and (4).

$$M(x/a; 0) = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{-(-1)^n}{n^2} \cos(n\pi x/a)$$

$$= \frac{1}{6} - \frac{1}{2}\left(\frac{x}{a}\right)^2 \qquad (4)$$

Equation (4) gives the value of $M(x/a; P)$ when $P = 0$. When $\theta = \infty$, equation (3) must reduce to

$$B(t-t_o) = \frac{P_1}{\pi^2} \qquad (5)$$

Equation (5) when solved for $t - t_o$ merely states that the temperature rise is the average temperature rise due to a total heat input of $q_m\theta_1$. Thus the temperature becomes independent of x. Equation (3) must also satisfy

$$\int_0^a (t-t_o) C\rho dx = \frac{b\theta_1^2}{2}.$$

Case II. Heating Period. Constant Heating Rate

At the start, the slab has the uniform temperature t_o and the constant heating rate over the face $x = a$ is q_m. Heating is abruptly dis-

continued at θ_1. The equation must satisfy conditions (a), (b), and (d) of Case I and

$$(c)\ \frac{\partial t}{\partial x} = \frac{q_m}{K} \text{ at } x = a$$

$$(e)\ \int_0^a (t - t_o) C\rho dx = \int_0^\theta q_m d\theta = q_m \theta$$

In this case $q_m = q$.

An equation, in dimensionless form, which satisfies all of these conditions is:

$$B(t - t_o) = \frac{P}{\pi^2} - \frac{1}{6} + \frac{1}{2}\left(\frac{x}{a}\right)^2 + M(x/a; P) \quad (6)$$

Case II. Temperature Equalizing Period

After the heating is stopped abruptly at $\theta = \theta_1$ the time-temperature relations are represented by the following equation (7), θ being measured from the beginning of the heating period:

$$B(t - t_o) = \frac{P_1}{\pi^2} + \left[M(x/a; P) - M(x/a; P - P_1) \right] \quad (7)$$

When $\theta = \theta_1$, $P = P_1$ and equation (7) must reduce to equation (6). By the use of equation (4) it is easy to show that this is true.

When $\theta = \infty$,

$$B(t - t_o) = P_1/\pi^2$$

showing the final equalizing of temperature, independent of x. Equation (7) must also satisfy $\int_0^a (t - t_o) C\rho dx = q_m \theta_1$.

Case III. Heating Period. Linearly Decreasing Heating Rate

At the start, the slab has the uniform temperature t_o and the heating rate is q_o. At any time θ, the heating rate is $q = q_o - b\theta$. At

time θ_1, $q_o = b\theta_1$ and $q_1 = 0$, representing the end of the heating period. The equation must satisfy conditions (a), (b), and (d) of Case I and

$$(c)\ \frac{\partial t}{\partial x} = \frac{q}{K} = \frac{q_o - b\theta}{K} \text{ at } x = a.$$

$$(e)\ \int_0^a (t - t_o) C\rho dx = \int_0^\theta (q_o - b\theta)\, d\theta = q_o\theta - \frac{b\theta^2}{2}$$

It is to be noted that $2q_m = q_o$.

An equation, in dimensionless form, satisfying all of these conditions is:

$$B(t - t_o) = \frac{2P}{\pi^2}\left(1 - \frac{1}{2}\frac{P}{P_1}\right) + \left[\left(\frac{x}{a}\right)^2 - \frac{1}{3}\right]\left(1 - \frac{P}{P_1}\right) + 2M(x/a; P)$$

$$- \left(\frac{P}{P_1}\right)\left(\frac{2\pi^2}{P}\right)\left[\frac{1}{24}\left(\frac{x}{a}\right)^4 - \frac{1}{12}\left(\frac{x}{a}\right)^2 + \frac{1}{24} - \frac{1}{45} - N(x/a; P)\right] \qquad (8)$$

Case III. Temperature Equalizing Period

After the heating is discontinued at $\theta = \theta_1$, the time-temperature relations are given by the following equation (9), θ being measured from the beginning of the heating period.

$$B(t - t_o) = \frac{P_1}{\pi^2} + 2M(x/a; P) + \frac{2\pi^2}{P_1}\left[N(x/a; P) - N(x/a; P - P_1)\right] \qquad (9)$$

When $\theta = \theta_1$ equation (9) must reduce to equation (8), and this can be shown to be true by the use of equation (2).

When $\theta = \infty$, the temperature becomes equalized and is independent of x. Under these conditions, equation (9) reduces to

$$B(t - t_o) = P_1/\pi^2$$

It also satisfies $$\int_0^a (t - t_o) C\rho dx = q_o\theta_1 - \frac{b\theta_1^2}{2}$$

Reduction to Numerical Values

Table 1 gives a set of values of the M- and N-functions at $x/a = 1$ and at $x/a = 0$ for a range of values of P from 0 — 12. For values of P greater than 12, these functions have negligible values and may be omitted from the equations. Equations (1), (6), and (8) represent the heating period in each case. Table 2 gives a set of numerical values of $P_1B(t - t_o)$ for Equation (1). In order to plot $B(t - t_o)$ against P, it is necessary to divide each of these values by the chosen value of P_1. Table 2 also gives values of $B(t - t_o)$ which can be plotted directly against P. Equation (8) requires different treatment, and a satisfactory graphical method of obtaining a plot of $B(t - t_o)$ is as follows: From the values in Table 3, plot $B(t - t_o)$ as ordinate against P. This gives two curves, for $P/P_1 = 0$ and 1.0. Divide the length of ordinate lying between the $P/P_1 = 0$ and the $P/P_1 = 1.0$ curves into ten equal parts at several values of P and plot the division points. Then lay off the nine curves through these points. Thus is obtained a family of eleven curves with equally spaced ordinates. Mark each curve with the value of P/P_1 which it represents. Then choose a numerical value for P_1 and it becomes obvious that one point on the final $B(t - t_o)$ vs. P curve will be the intersection of the ordinate at P_1 with the $P/P_1 = 1.0$ curve. The ordinate at $P = 0.9\,P_1$ will intersect the $P/P_1 = 0.9$ curve at the next point on the final curve. By repeating this operation, one finally works back to the origin, and the eleven intersections (including the origin) can be connected by a smooth curve which is the final solution. This method is shown

in Figure 1. Equations (3), (7), and (9) represent the equalizing period in each case. It is not possible to present any useful tables of values of $B(t - t_o)$ for these equations, but it is a very simple

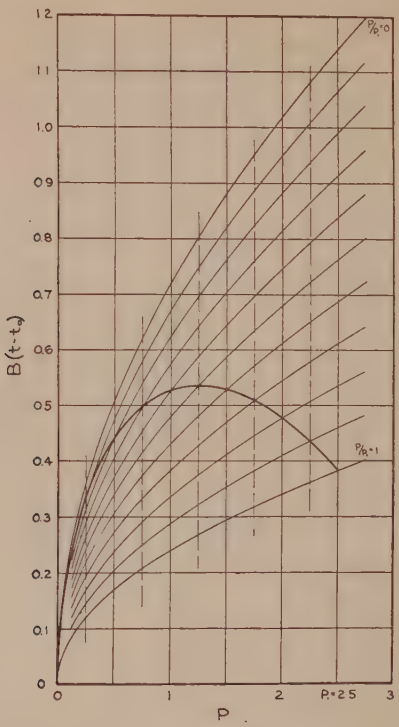

FIG. 1. The construction of the B $(t-t_o)$ vs. P curves for $x/a = 1$ in the decreasing rate case.

matter to construct a table once a value of P_1 has been selected, by utilizing Table 1.

The selection of a value of P_1 requires some consideration. Ordinarily the conditions of the practical problem will dictate a maximum value for the ratio of maximum temperature rise at the face to the accomplished temperature rise at the center.

TABLE 1

P	x/a = 1		x/a = 0	
	—M(x/a; P)	—N(x/a; P)	M(x/a; P)	N(x/a; P)
0.0	0.333333	0.022222	0.166667	0.019444
0.1	0.229885	0.019561	0.156535	0.017807
0.2	0.192970	0.017432	0.146403	0.016272
0.3	0.167002	0.015615	0.136276	0.014840
0.4	0.146700	0.014029	0.126202	0.013511
0.5	0.130019	0.012630	0.116298	0.012282
0.6	0.115911	0.011386	0.106718	0.011153
0.7	0.103751	0.010274	0.097590	0.010118
0.8	0.093135	0.009278	0.089005	0.009173
0.9	0.083779	0.008383	0.081011	0.008313
1.0	0.075479	0.007577	0.073623	0.007530
1.5	0.045341	0.004584	0.045095	0.004578
2.0	0.027442	0.002779	0.027408	0.002778
2.5	0.016636	0.001685	0.016632	0.001685
3.0	0.010089	0.001022	0.010088	0.001022
3.5	0.006119	0.000620	0.006119	0.000620
4.0	0.003712	0.000376	0.003712	0.000376
4.5	0.002251	0.000228	0.002251	0.000228
5.0	0.001365	0.000138	0.001365	0.000138
5.5	0.000828	0.000084	0.000828	0.000084
6.0	0.000502	0.000051	0.000502	0.000051
6.5	0.000305	0.000031	0.000305	0.000031
7.0	0.000185	0.000019	0.000185	0.000019
7.5	0.000112	0.000011	0.000112	0.000011
8.0	0.000068	0.000007	0.000068	0.000007
8.5	0.000041	0.000004	0.000041	0.000004
9.0	0.000025	0.000002	0.000025	0.000002
9.5	0.000015	0.000002	0.000015	0.000002
10.0	0.000009	0.000001	0.000009	0.000001
10.5	0.000006	0.000001	0.000006	0.000001
11.0	0.000003	0.000000	0.000003	0.000000
11.5	0.000002	0.000000	0.000002	0.000000
12.0	0.000001	0.000000	0.000001	0.000000

TABLE 2

P	$P_1B(t—t_o)$ For Eq. (1)		$B(t—t_o)$ For Eq. (6)	
	x/a = 1	x/a = 0	x/a = 1	x/a = 0
0.0	0.0000	0.0000	0.0000	0.0000
0.1	0.0152	0.0000	0.1136	0.0000
0.2	0.0428	0.0000	0.1606	0.0000
0.3	0.0787	0.0000	0.1967	0.0000
0.4	0.1212	0.0000	0.2272	0.0001
0.5	0.1693	0.0002	0.2540	0.0003
0.6	0.2226	0.0005	0.2782	0.0008
0.7	0.2805	0.0014	0.3005	0.0018
0.8	0.3427	0.0029	0.3213	0.0034
0.9	0.4099	0.0050	0.3407	0.0055
1.0	0.4789	0.0079	0.3592	0.0083
1.5	0.8799	0.0357	0.4400	0.0304
2.0	1.3548	0.0845	0.5085	0.0634
2.5	1.8945	0.1505	0.5700	0.1033
3.0	2.4934	0.3055	0.6272	0.1474
3.5	3.1481	0.4461	0.6818	0.1941
4.0	3.8566	0.6643	0.7349	0.2423
4.5	4.6176	0.9311	0.7870	0.2915
5.0	5.4304	1.2474	0.8386	0.3413
5.5	6.2947	1.6138	0.8898	0.3914
6.0	7.2099	2.0304	0.9408	0.4418
6.5	8.1761	2.4974	0.9916	0.4922
7.0	9.1931	3.0148	1.0424	0.5428
7.5	10.2608	3.5829	1.0931	0.5934
8.0	11.3794	4.2016	1.1438	0.6440
8.5	12.5486	4.8709	1.1945	0.6946
9.0	13.7684	5.5908	1.2452	0.7452
9.5	15.0390	6.3622	1.2959	0.7959
10.0	16.3602	7.1826	1.3465	0.8466
10.5	17.7320	8.0545	1.3972	0.8972
11.0	19.1549	8.9773	1.4479	0.9479
11.5	20.6281	9.9506	1.4985	0.9986
12.0	22.1520	10.9744	1.5492	1.0492

TABLE 3

Values of $B(t-t_o)$ for Equation (8).

P	x/a = 1		x/a = 0	
	$P/P_1 = 0.0$	1.0	0.0	1.0
0.0	0.0000	0.0000	0.0000	0.0000
0.1	0.2272	0.0756	0.0000	0.0000
0.2	0.3213	0.1071	0.0000	0.0000
0.3	0.3935	0.1311	0.0000	0.0000
0.4	0.4543	0.1514	0.0001	0.0001
0.5	0.5079	0.1693	0.0006	0.0005
0.6	0.5564	0.1855	0.0015	0.0014
0.7	0.6010	0.2003	0.0037	0.0031
0.8	0.6425	0.2142	0.0068	0.0056
0.9	0.6815	0.2272	0.0111	0.0091
1.0	0.7183	0.2394	0.0166	0.0134
1.5	0.8799	0.2934	0.0608	0.0465
2.0	1.0171	0.3397	0.1268	0.0930
2.5	1.1400	0.3822	0.2065	0.1464
3.0	1.2544	0.4233	0.2948	0.2029
3.5	1.3637	0.4642	0.3381	0.2607
4.0	1.4698	0.5057	0.4847	0.3186
4.5	1.5741	0.5479	0.5831	0.3762
5.0	1.6771	0.5911	0.6826	0.4331
5.5	1.7795	0.6351	0.7829	0.4894
6.0	1.8815	0.6799	0.8835	0.5451
6.5	1.9832	0.7254	0.9845	0.6003
7.0	2.0848	0.7715	1.0855	0.6548
7.5	2.1863	0.8181	1.1867	0.7090
8.0	2.2877	0.8652	1.2879	0.7627
8.5	2.3890	0.9127	1.3892	0.8162
9.0	2.4904	0.9606	1.4905	0.8693
9.5	2.5917	1.0087	1.5918	0.9221
10.0	2.6931	1.0571	1.6931	0.9750
10.5	2.7944	1.1056	1.7944	1.0273
11.0	2.8957	1.1544	1.8957	1.0797
11.5	2.9970	1.2034	1.9971	1.1320
12.0	3.0984	1.2524	2.0984	1.1839

This ratio is plotted against P_1 in Figure 2. The accomplished temperature rise at the center is taken as P_1/π^2, the value of $B(t - t_o)$ when the temperature has become equalized. Of course, this condition is not actually realized at finite times, but the resulting curves give a rough guide in the selection of a value for P_1. One will use a value of P_1 based upon the selection of a somewhat lower temperature rise ratio than the maximum allowable value. Once a value of P_1 has been selected, the plotting of $B(t - t_o)$ vs. P curves for the heating and

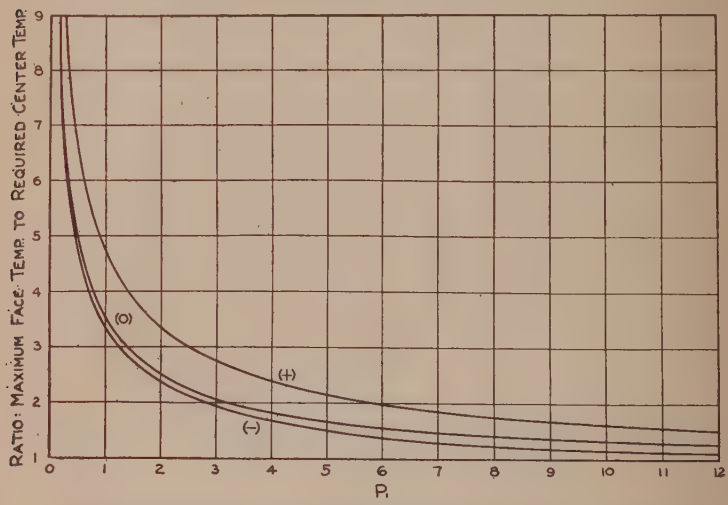

FIG. 2. Curves for the approximate selection of P_1 for the desired ratio of maximum face temperature to required center temperature.

equalizing range in all three cases is not laborious if the values in Tables 1, 2, and 3 are used; in order to avoid interpolation, it will be found desirable to select a value of P_1 equal to one of the values of P in Table 1.

Numerical Example

A slab of composition material 4 inches thick, initially at the uniform temperature 60° F. is to be heated electrically at its two faces to accomplish a temperature of 200° F. at the central plane. The face temperature should not rise above 400° F. Plot temperature-time curves for the faces and the central plane for the case of linearly

decreasing heating rate and compare with curves for the other two heating-rate cases. Data: $K = 0.09 \frac{\text{B.T.U. ft.}}{\text{ft.}^2\,^\circ\text{F. hr.}}$; $k = 0.003$ ft.^{2}/hr.; $a = 1/6$ ft.

The following solution of the problem uses the decreasing rate case as a basis. For comparison, the solution of the other two cases is based upon the same average heat-input rate and the same length of heating period.

Maximum rise at faces $= 400^\circ - 60^\circ = 340^\circ$. Required rise at

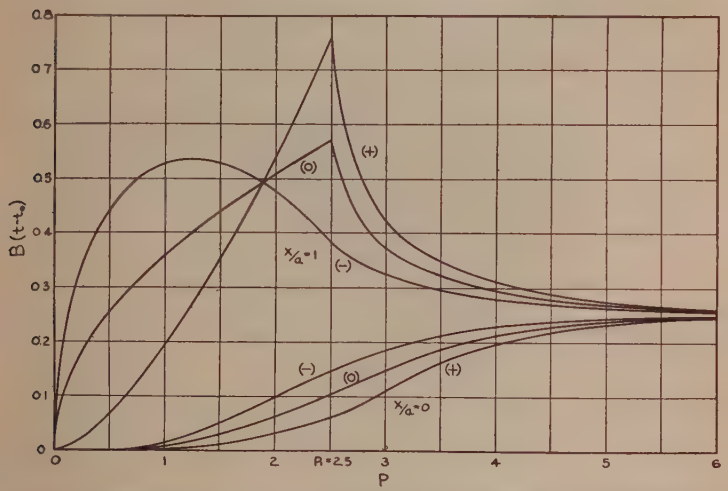

FIG. 3. Curves for $B(t-t_0)$ vs. P for the three heating cases, showing the heating and equalizing periods, for the selected value of $P_1 = 2.5$.

center $= 200^\circ - 60^\circ = 140^\circ$. Ratio $= 340/140 = 2.43$. Figure 2 gives $P_1 = 2.15$ for ratio $= 2.43$. As this figure is based upon complete temperature equalization in obtaining desired center temperature, a larger value of P_1 should be chosen. Selecting $P_1 = 2.5$ for the three cases, Figure 3 shows the final curves. (+), (0) and (—) are marked on the curves, indicating increasing, constant and decreasing rate, respectively. For each case, the upper curve is for the heated faces and the lower curve is for the center.

Case III (Decreasing Rate). The maximum value of $B(t - t_0)$ at the heated face, read from the curve, is 0.535;

$B = 0.535/(t - t_o) = 0.535/340 = K/q_m a$. Substituting the known values of K and a, $q_m = 343$ B.T.U./ft.^{2} hr. At the center, $t - t_o = 140$ and $B(t - t_o) = (0.535)(140)/340 = 0.22$, and from Figure 3 we find $P = 3.7 = \pi^2 k\theta/a^2$. Substituting known values of k and a^2, $\theta = 3.47$ hours. Also $P_1 = 2.5 = \pi^2 k\theta_1/a^2$, giving $\theta_1 = 2.34$ hours.

Case II (Constant Rate). The maximum value of $B(t - t_o)$ at the heated face is read from Figure 3 as 0.57. $q_m = 343$ and $B = 0.535/340$, as in Case III. As $B(t - t_o) = 0.57$, $t - t_o = 0.57/B = 362°$, and the maximum face temperature is $362° + 60° = 422°$. At the center, $B(t - t_o) = 0.22$ as in Case III, and Figure 3 gives $P = 4.23$, from which $\theta = 3.97$ hours is computed.

Case I (Increasing Rate). The maximum value of $B(t - t_o)$ at the heated face is read from Figure 3 as 0.76. $q_m = 343$ and $B = 0.535/340$, as in Case III. As $B(t - t_o) = 0.76$, $t - t_o = 0.76/B = 482°$, and the maximum face temperature is $482° + 60° = 542°$. At the center, $B(t - t_o) = 0.22$ and Figure 3 gives $P = 4.55$, corresponding to $\theta = 4.27$ hours.

Comparison of the Three Cases

	I	II	III
Initial Heating Rate in B.T.U./ft.^{2}hr.	000	343	686
Final Heating Rate in B.T.U./ft.^{2}hr.	686	343	000
Average Heating Rate in B.T.U./ft.^{2}hr.	343	343	343
Length of Heating Period, in hours	2.34	2.34	2.34
Maximum Temp. at Faces, in °F.	542	422	400
Accomplished Temp. at Center	200	200	200
Time to Reach Accomplished Temp. at Center, in hours	4.27	3.97	3.47

The above summary shows that the best results are obtained by the use of a decreasing heat input rate. This method gives quicker heating at the center with a lower maximum surface temperature. If desired, the ordinate and abscissa axes of Figure 3 can be reproportioned into temperature-rise and time units.

Acknowledgment

The writer wishes to acknowledge the capable assistance rendered by A. Gelbart and L. Green, who computed the values given in Table 1.

Discussion

A. B. Newman (communicated) : This paper has introduced some unusual mathematical functions, which have been identified by Dr. H. T. Davis, Professor of Mathematics in Indiana University, and author of : Tables of the Higher Mathematical Functions, Vol. 1 (1933), The Principia Press, Bloomington, Ind. From his letter:

> "You will be interested to know that your M and N functions are actually the second and fourth integrals of one of the theta functions. This you will see if you replace e^{-P} by v and compare with the definitions given in Jahnke and Emde's 'Funktionentafeln.' I do not know of any other tables of these integrals. The fifth volume of my series will contain elaborate tables of elliptic integrals and of elliptic and theta functions. I shall be particularly glad to include these values of yours in this volume with a description of their properties and usefulness. M(z,0) and N(z,0) together with their generalizations are evaluated in terms of Bernoulli polynomials. Quite extensive tables of these polynomials appear in my second volume which is now ready for press."

CHEMICAL ENGINEERING LABORATORY DEMONSTRATIONS

SOME NEW DEVELOPMENTS

By CHARLES R. JOHNSON *

It is a well-known fact that when the average person performs an experiment by himself, or watches another perform it, a more lasting impression is obtained for future reference than would be derived from a study of a text describing the experiment. For this reason instruction in certain branches of science is relatively simple, for, although a person may not know what friction is, for example, the chances are that he has experienced difficulty in walking over an icy surface, or has brought his automobile to a stop by use of the brakes, or has noticed how much easier two metal surfaces slide over each other when a little oil is placed between them. In other words, when friction is mentioned, he immediately conjures up a mental picture of the effects produced by it, and as a result the subject seems familiar and nothing to be feared.

In chemistry and chemical engineering, on the other hand, there are few people who have had a chance to see the fundamentals of these sciences in action, and, therefore, they lack a mental picture to aid them in understanding the most simple of their concepts. For this reason it is not only desirable but essential, that the student have adequate opportunity to either perform actual experiments by himself, or see them performed as lecture demonstrations.

Laboratory instruction, however, has its disadvantages, for, while it affords excellent instruction in actual performance it requires a large and varied supply of equipment especially when sizable classes are being taught. Furthermore the average student is so poorly developed in experimental technique, that it is impossible for him to perform any large number of experiments in the time available. Therefore it is necessary to supplement laboratory instruction with lecture demonstrations.

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A well designed lecture experiment should be simple, illustrative of but one point or fact, novel, quantitative if possible, and should give the student instruction in the proper methods of performing such work. Fortunately chemical engineering experiments can be made to conform to all these requirements.

At the Massachusetts Institute of Technology a concerted effort has been made, during the last few years, to develop a set of lecture experiments for presentation to the students taking Undergraduate Chemical Engineering. Not only have the experiments been designed to comply with the requirements stated above, but an attempt has also been made to use apparatus that is as crude as possible to illustrate that elaborate equipment is not essential for good results. Also in making the experiments quantitative, it has been possible to test the accuracy of the formulas presented in the text book, and thereby give the students confidence in the results obtained by using them.

In the presentation of the lecture experiments the following procedure has been found to give satisfactory results. The experiments are designed, assembled, and given a try-out by the assistant in the course previous to the actual lecture demonstration. This serves to acquaint the assistant with the operating characteristics of the apparatus, and oftentimes exposes undesirable features which are then eliminated. At the start of the lecture the purpose of the experiment is explained by the instructor, who then gives a detailed description of the apparatus and operating procedure. The experiment is then performed by the assistant with the aid of student helpers, and the data taken. These data are then tabulated and presented to the class as the basis of a problem, or else the instructor, using the blackboard, analyzes the data and compares the results actually obtained with results calculated by the use of formulas. This is all done within the time of one hour.

In order to illustrate the type of experiments used, a few typical ones are described below.

Experiment 1

Object: To show the amount of pressure head lost when using an orifice meter or a Venturi meter.

Apparatus: The orifice was made from two pieces of 2″ copper pipe, one 12″ long for the upstream section, and the other 36″ long for the downstream section. To one end of each section was soldered

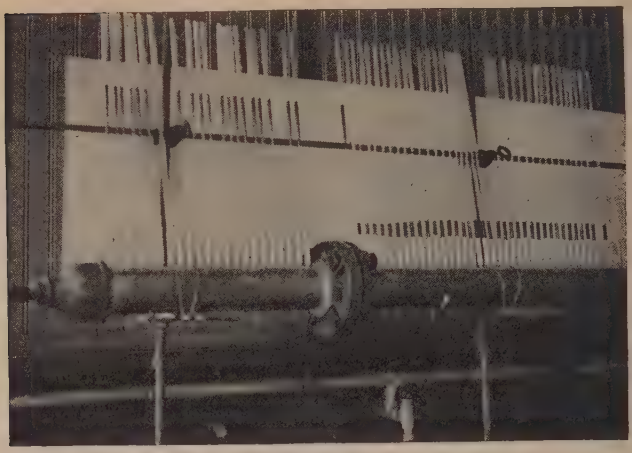

FIG. 1

FIG. 2

a 2″ to ¾″ reducing coupling, and into these were screwed ¾″ to ⅜″ reducing bushings and short ⅜″ nipples. To the other end of each section was soldered one part of a 2″ flanged union. The orifice plate was made from a piece of galvanized iron, and drilled with a 5/16″ hole. When this was inserted between the flanges of the union, the joint was made tight by the use of rubber gaskets. Along one side of the copper pipe were drilled ⅛″ holes, and these were countersunk to accommodate short pieces of 3/16″ copper tubing. Glass standpipes 1′ in length were then connected to these by means of rubber connectors.

FIG. 3

The Venturi device was made from sheet copper with upstream and downstream sections 2″ in diameter and 6″ long. The throat was made from a piece of brass rod 1″ long in which was drilled a ½″ hole the ends of which were beveled to fit the section ends as well as possible. The upstream reduction section was 3-7/16″ long and the downstream enlargement section was 12-3/16″ long. The standpipes were connected as before.

Results: The results are well illustrated by Figures 1 and 2. With the orifice, the reading was well over 6″ and the lost head was over 90%, while with the same reading on the Venturi the lost head was only about 25%.

Experiment 2

Object: To show friction loss in a pipe.

Apparatus: A 20′ length of ¼″ iron pipe was cut into two 9′ and two 1′ sections. These were assembled in the shape of a U through the use of two 90° elbows and a union, and Figure 3 shows the ends of the U. Piezometer rings, made from copper tubing and short brass nipples, were attached to the ends of the pipe by ¼″ couplings, and a differential mercury manometer installed, care being taken to see that the leads were filled with water. Water was passed through the pipe and its rate was measured by timing the flow into a calibrated pail, during which period manometer readings were taken.

Results: Run 1 Actual reading=3.66 ft. water.
Calculated reading=3.68 ft. water.
Run 2 Actual reading=7.45 ft. water.
Calculated reading=7.66 ft. water.

Data: Run 1 Differential=3.5″ Hg; Rate=22 lbs./2.75 mins.
Run 2 Differential=7.1″ Hg; Rate=22 lbs./1.82 mins.

Water temperature 70°F.
Pipe—¼″ std., 20′ long, plus 2 elbows and 1 union.
Internal diameter 0.360″.

Calculations:

Run #1

$$\text{Cross section} = 0.785 \times \left(\frac{0.360}{12}\right)^2 = 0.000707 \text{ sq. ft.}$$

$$\text{Relative viscosity water} = 0.95$$

$$\text{Equiv. length} = 20 + \frac{0.360 \times 30 \times 2}{12} = 21.80 \text{ ft.}$$

$$\text{Re} = \frac{0.360 \times 22}{12 \times .000672 \times 2.75 \times 60 \times .000707 \times .95} = 8870$$

$$f = 0.0091$$

$$u = \frac{22}{2.75 \times 60 \times 62.5 \times .000707} = 3.0 \text{ ft./sec.}$$

$$h = \frac{2 \times .0091 \times 21.80 \times (3.0)^2 \times 12}{32.2 \times .360} = 3.68' \text{ water}$$

$$\text{Actual} = \frac{3.5 \times 12.6}{12} = 3.66' \text{ water}$$

Experiment 3

Object: To illustrate a simple apparatus for heating air by means of steam.

Apparatus: In this experiment the air was first passed through a large household gas meter to measure its rate of flow, and then

FIG. 4

through a ⅜" iron-pipe-size copper pipe having a heated length of 4'10". This pipe was surrounded by a 40 mm. glass tube which served as a jacket into which steam was passed. Four connections of 6mm. glass tubing were made to the jacket—one on the top and bottom of each end. The two bottom connections were used to draw off condensate, and the two top connections were used for steam supply and air vent respectively. The steam boiler consisted of a gallon can, with standpipe, heated on a table burner. The entrance air temperature was taken from a thermometer located immediately after the gas meter, and the exit temperature from a thermometer located in an insulated tee at the end of the heated pipe. See Figure 4.

Results: The results are shown plotted as $\frac{hD}{k}$ vs. $\frac{DG}{\mu}$ (consistent units) in Figure 5. The line AA shown on the plot is that recommended by McAdams on page 172 of his book on "Heat Transmission," and it is seen that the present data compares favorably with that taken by previous investigators.

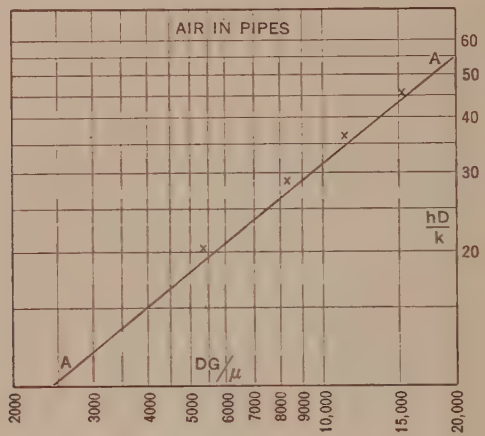

FIG. 5

Data: Heated length 4′ 10″.

Internal diameter of pipe 0.494″.

Run	T_1 °C	T_2 °C	Cu. ft./min.
1	22.1	92.4	1.85
2	22.0	90.75	2.88
3	22.0	89.2	3.86
4	22.0	87.45	5.17

Steam temperature 100° C.
Average specific heat 0.24.

Experiment 4

Object: To compare heat losses by convection and radiation from a steam pipe to a room.

Apparatus: For this experiment the same pipe was used as in Experiment 2. The steam was supplied from the gallon can boiler and passed through a short piece of 5/16″ copper tubing under which

was placed a gas burner as shown in Figure 6 so that the steam could be slightly superheated. A thermometer placed in a glass tee at the entrance of the pipe gave the entering steam temperature. The pipe was slanted throughout its length so that the condensate would drain properly and the latter was caught in a beaker and weighed. A small amount of steam was allowed to escape from the outlet end continuously.

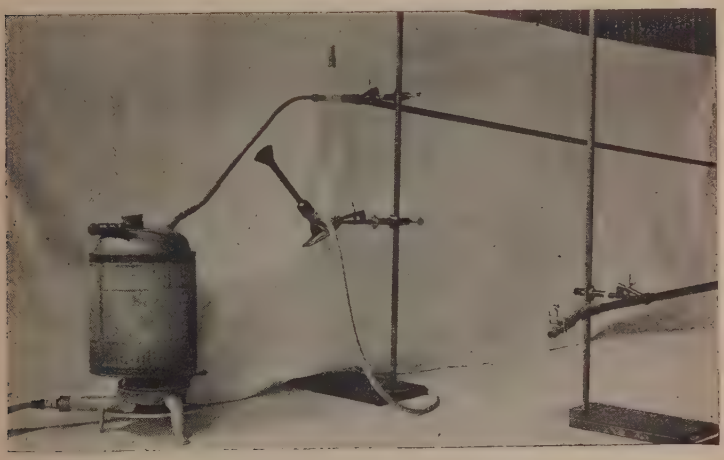

FIG. 6

Results: Calculated heat loss = 0.341 B.T.U./sec.
Measured heat loss =0.35 B.T.U./sec.

Data: Temperature inlet steam = 103° C.
Condensate = 196.5 grams in 20 minutes.
Pipe length = 20 ft. 2 inches.
External pipe diameter = 0.54 inches.
Room temperature = 21.5° C. or 71° F.

Calculations:

$$\text{Outside area} = \frac{0.54}{12} \times 3.14 \times 20.17 = 2.85 \text{ sq. ft.}$$

Pipe temperature was assumed to be 212° F.

$$h'' \text{ convection} = \frac{0.225}{3600}\left(\frac{\triangle t}{d}\right)^{1/4} \text{ where } \triangle t = 141° \text{ F.}$$

$$\therefore h'' = \frac{0.225}{3600}\left(\frac{141 \times 12}{0.54}\right)^{1/4} = 0.000467.$$

$$\frac{Q''}{\theta} \text{ convection} = 0.000467 \times 2.85 \times 141 = 0.188 \text{ B.T.U./sec.}$$

$$\frac{Q''}{\theta} \text{ radiation} = \frac{0.172 \times 0.9 \times 2.85}{3600}\left[\left(\frac{672}{100}\right)^4 - \left(\frac{531}{100}\right)^4\right]$$

$$= 0.153 \text{ B.T.U./sec.}$$

$$\text{Total calculated loss} = 0.188 + 0.153 = 0.341 \text{ B.T.U./sec.}$$

$$\text{Actual loss} = \frac{196.5}{454} \times 970 \times \frac{1}{20 \times 60} = 0.350 \text{ B.T.U./sec.}$$

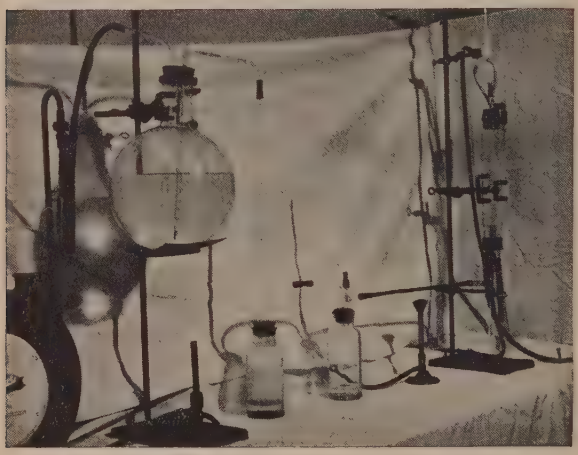

FIG. 7

Experiment 5

Object: To investigate the path on the humidity chart taken by air during dehumidification.

Apparatus: Air was passed first through a wet gas meter and then through a 5-liter flask partially filled with water, the temperature of the latter being controlled by a gas burner. Next the air was passed through two common bottles in series, the object being to cool it somewhat so that the temperature measured at the outlet

would represent both the wet and dry bulb readings. The air was then heated by passing it through a short length of copper tubing which was heated by a gas burner, after which it entered the bottom of the dehumidifying tower.

This was made from a piece of 1¾″ inside diameter glass tubing 12″ long. Water was sprayed onto the walls by means of a distributing device, the rate being high enough so that the temperature

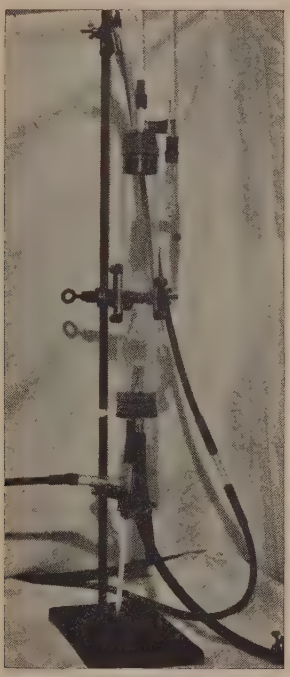

Fig. 8

remained substantially constant. A dry bulb reading of the entering heated air and wet and dry bulb readings of the cool exit air were taken, and radiation losses were lessened by using a high air velocity past the bulbs of the thermometers.

For further details see Figures 7 and 8.

Results: Figure 9 shows the data plotted on an enlarged humidity chart, and it is clearly demonstrated that during dehumidification air does not become saturated.

Experiment 6

Object: To illustrate the operation of a triple effect evaporator.

Apparatus: For the first effect a 5-liter flask heated by a gas burner was used. This was fitted with a standpipe, a thermometer, and a vapor line leading to the second effect. For the second and third effects, one-gallon bottles were fitted with heating coils made from 3/16″ copper tubing 18″ in length. Each was also equipped with a thermometer, a vapor line, and one extra connection for ease in filling and emptying. The vapors from the first and second effects

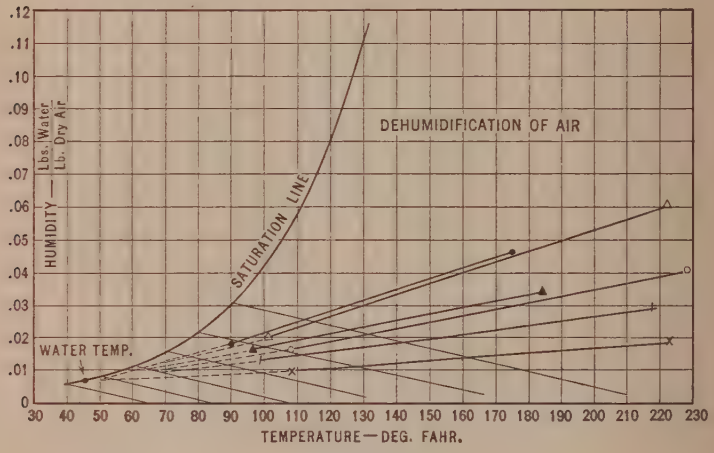

FIG. 9

were, of course, condensed in their succeeding effect, while the vapors from the third effect were condensed in an ordinary short tube condenser. The condensates from the three effects were caught in calibrated common bottles, which also had connections leading to a manometer board and vacuum line. Figure 10 shows the apparatus as assembled.

Results: The apparatus gave very satisfactory performances, and would run for over an hour before refilling was necessary. Just before the experiment was shown the effects were filled with hot water which considerably lessened the time necessary to get all of the effects into operation.

Other experiments performed during the course illustrated such points as Bernoulli's Theorem; conduction, convection, and radiation of heat; effect of gas films on heat transfer; water to water heat exchanger; errors in temperature measurement due to radiation; drying; extraction; crushing and grinding; mechanical separation; filtration; and distillation.

The above experiments, while relatively simple in their construction and operation, were found to be well worth while because of the manner in which they impressed the students with the facts

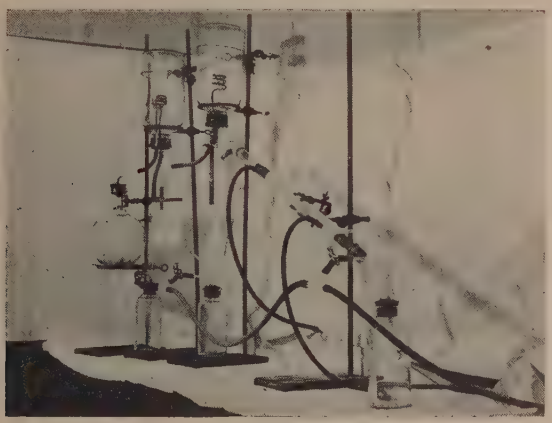

FIG. 10

and theories of chemical engineering. The excellent agreement between the data and results calculated by the use of formulas, helped considerably to give the students confidence in the latter. In addition, the various operations performed during the course of the experiments showed them certain features of experimental technique which will be of value to them when they undertake research work of their own.

Acknowledgment

I wish to express my appreciation for the interest and encouragement of Prof. C. S. Robinson, and the late Prof. W. P. Ryan.

A.I.CH.E. ANNUAL STUDENT COMPETITION

Foreword

The third annual student competition was sponsored in 1934 under the direction of the Committee on Student Chapters, A. McLaren White of the University of North Carolina, Chairman, and the Sub-Committee on Awards—Professor T. K. Sherwood, Massachusetts Institute of Technology, Chairman; Drs. Thomas H. Chilton and Allan P. Colburn, E. I. duPont deNemours Company, Wilmington, Delaware.

Thirty-five solutions were submitted representing seventeen chapters. The rules of the competition preclude submission of more than three solutions from any one chapter.

On the recommendation of the Committee on Awards Council awarded prizes as follows: 1st prize of $100.00 to Robert V. Lukes, University of Illinois, Urbana, Illinois; 2nd prize of $50.00 to Scott Lyon, Ohio State University, Columbus, Ohio; and 3rd prize of $25.00 to Waldemar A. Schmidt, Oregon State Agricultural College, Corvallis, Oregon. Through the courtesy of Mr. James S. Thompson, Vice-President of the McGraw Hill Book Company 4th and 5th prizes of copies of Perry's Handbook of Chemical Engineering were awarded to Albert E. New, University of North Carolina and David C. Grahame, University of Minnesota, respectively.

As is customary the 1st prize winning solution is published in the Transactions.

Frederic J. LeMaistre,
Secretary

CONTEST PROBLEM

1934

National Student Competition Sponsored by the American Institute of Chemical Engineers Under the Direction of the Committee on Student Chapters
(Open to Undergraduates Only)

Statement

The plant proposes to install filters, either of the chamber or of the leaf type, to handle 30,000 gallons per day of a slurry yielding a homogeneous cake (no filter aids are necessary). A test on a small filter press having a cross section of 1 sq. ft. shows that 37 gals. of slurry are filtered in 7 hrs., 10 min., when operating in such a way that 18½ gal. of the filtrate came through at constant rate and the remainder at a constant pressure. During the operation at constant filter rate, the pressure is increased gradually to 60 lbs./sq. in. gauge, which is the pressure employed in the subsequent constant pressure operation. The resulting cake fills a 1 in. distance frame (i.e., 1 sq. ft. of frame or actually 2 sq. ft. of cloth, giving a cake thickness of ½ in. on each filter cloth).

When installed, the presses are to operate at constant rate until the pressure has reached 50 lbs./sq. in. gauge, after which the pressure is maintained constant for the remainder of the cycle. It will be assumed that the rate, as cubic feet per hour per square foot of cloth, during the constant rate period, will be 50% greater than that prevailing during the constant rate portion of the test described, and that the coefficient of compressibility "s" (see Walker, Lewis & McAdams, second edition, page 363) may be taken as 0.1. It is proposed to wash the cake with water equal in volume to one-third of the volume of the filtrate after each filtering cycle. With the chamber press this will be done from one filter leaf to the next through the entire cake thickness, but in the leaf filter in the same direction as the filtrate is passed. Time for cleaning and reassembling will be 2.5 hours per press for the chamber type, and 45 minutes per press for the leaf type. Supervision will be independent of press size and type, but labor for cleaning costs 60c/hr./press. The maximum size of single units of either type will be 900 sq. ft., and when two or more

presses are necessary they will be of equal size. The installed first cost per sq. ft. of filtering area is given below:

Size, sq. ft.	100	300	500	700	900
Chamber	$4.90	3.00	2.50	2.30	2.10
Leaf	14.00	11.00	9.60	8.50	7.50

Fixed charges may be taken as 30% per year of 330 days and operation 24 hours per day. Filter cloth costs 11 cents per sq. ft., and may be cleaned 60 times.

Specify the optimum size and operating cycle for (a) the chamber press, and (b) the leaf type.

Calculate the difference in annual costs of the most economical installations of each type.

NOTE: It should be noted that for a filtration conducted as described, the integrated filtration equations given in Walker Lewis & McAdams, 2nd Edition, page 366, cannot be applied directly but must be derived from the differential equation with substitution of the appropriate limits.

Method of Presentation

The solution of this problem should be presented as a report recommending the type and size of filter press to be purchased. In grading reports significance will be given to the form of presentation as well as to the accuracy of the assumptions and computations. Assumptions made should be clearly indicated.

Assume that the decision on expenditure will be made by an executive who has had technical training but is not familiar with modern chemical engineering developments. This executive will require that his technical assistant check the accuracy of the assumptions, calculations, and results in the report. However, in weighing the recommendation and reaching a decision he wants to assure himself personally of the basis for computation and of the validity of the economic method employed. His available time is limited and not more than three minutes of his attention should be required.

FIRST PRIZE WINNING SOLUTION CONTEST PROBLEM

1934

STUDENT CHAPTERS
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

on

THE PROPOSED INSTALLATION OF FILTER PRESSES

ROBERT V. LUKES
University of Illinois

SUMMARY AND RECOMMENDATIONS

The optimum size of each type of filter press has been taken as that which gives the minimum total annual cost. The results found are here tabulated:

Type of Press	Size of Single press Sq. ft.	Number of Presses	Operating cycle Hrs.	ANNUAL COSTS			
				Fixed charges $/yr.	Filter cloth $/yr.	Cleaning and Reassembling $/yr.	Total $/yr.
Chamber....	900	3	61.71	1710	635	577.50	2922.50
Leaf.....	900	1	14.46	2026	904	246.30	3176.30
Difference in annual costs.....							$253.80

DISTRIBUTION OF TIME DURING OPERATING CYCLES IN HOURS

Type of Press	Filtration at constant rate	Filtration at constant press.	Washing	Cleaning and Reassembling	Total
Chamber.....	1.11	15.5	42.6	2.5	61.71
Leaf.....	1.11	7.34	5.26	0.75	14.46

The chamber presses would require 1½ inch distance frames. The cake thickness in the leaf press would be 0.543 inches.

The results indicate that the most economical installation would consist of three 900 sq. ft. chamber type presses with 1½ inch distance frames. The total annual cost of this installation would be

$253.80 less than the most economical installation of the leaf type of press.

Test Filtration

37 gals. of slurry filtered in 7 hrs., 10 min.

18.5 gals. of filtrate at constant rate and remainder at constant pressure.

37 gals. of slurry yield $\frac{1}{12} \times 1 \times 1 = \frac{1}{12}$ cu. ft. of cake

$$\frac{1}{12} \text{ cu. ft.} = \frac{7.48}{12} \text{ gal.} = 0.623 \text{ gal. of cake.}$$

Therefore there are:

0.01684 gal. of cake per gal. of slurry
or 0.9832 gal. of filtrate per gal. of slurry;

$37 - 0.623 = 36.377$ gal. of filtrate during the test.

The total press area was 2 sq. ft.; therefore the total volume of filtrate is 18.19 gal. per sq. ft. of press area and the total volume of filtrate at the end of the constant rate period is:

$$\frac{18.5}{2} = 9.25 \text{ gal. per sq. ft. of press area.}$$

The differential equation for a homogeneous compressible sludge is:

$\frac{dV}{d\theta} = \frac{P^{1-s}A^2}{r'vV}$; which can be written in the form

$\frac{d\left(\frac{V}{A}\right)}{d\theta} = \frac{P^{1-s}}{r'v\left(\frac{V}{A}\right)}$; where $\frac{V}{A}$ is the total vol. of filtrate in gal. coming out of the press in time θ.

Integrating the above equation:

$$\int_0^{\theta} d\theta = \int \left[\frac{r'v}{P^{1-s}} \left(\frac{V}{A}\right) d\left(\frac{V}{A}\right) \right] + C = \theta_1 + \theta_2$$

Where

θ is the time, in hrs., up to the end of the filtration
θ_1 is the length of time of the const. rate period
θ_2 is the length of time of the const. pressure period.

For constant rate:

$$\frac{V}{A\theta} = \frac{P^{1-s}}{r'v\left(\frac{V}{A}\right)} = \text{constant}$$

$$\theta = \int_0^{9.25} \left(\frac{1}{\frac{V}{A\theta}}\right) d\left(\frac{V}{A}\right) + \frac{r'v}{P^{1-s}} \int_{9.25}^{18.19} \frac{V}{A}\, d\left(\frac{V}{A}\right)$$

$$\theta = r'v\left[\frac{\left(\frac{V}{A}\right)}{P^{1-s}}\right]^{*} \int_0^{9.25} d\left(\frac{V}{A}\right) + \frac{r'v}{P^{1-s}} \int_{9.25}^{18.19} \left(\frac{V}{A}\right) d\left(\frac{V}{A}\right)$$

$$\theta = r'v\, \frac{9.25}{(60)^{0.9}} \times \frac{V}{A}\Bigg]_0^{9.25} + \tfrac{1}{2}\, \frac{r'v}{60^{0.9}} \left(\frac{V}{A}\right)^2 \Bigg]_{9.25}^{18.19}$$

$$\theta = r'v\, \frac{(9.25)^2}{(60)^{0.9}} + \frac{1}{2} \times \frac{r'v}{60^{0.9}} \times (18.19^2 - 9.25^2)$$

$$\theta = 2.147r'v + 3.077r'v = \theta_1 + \theta_2$$

But $\theta = 7.1667$ hrs.

Therefore:

$$5.224r'v = 7.1667$$
$$r'v = 1.372$$

Therefore $\theta_1 = 2.147 \times 1.372 = 2.945$ hrs.
and $\theta_2 = 3.077 \times 1.372 = 4.222$ hrs.

---

* Simultaneous values of P and $\frac{V}{A}$ must be substituted here in order to evaluate the const. rate.

The general filtration equation expressing the test as conducted therefore is:

$$\theta = \frac{1}{R} \times \frac{V}{A} + \frac{1}{2} \times \frac{r'v}{P^{1-s}} \left[\left(\frac{V}{A} \right)^2 - \left(\frac{V_1}{A} \right)^2 \right]$$

Where R is the rate of filtration in gal. per hr. per sq. ft. during the constant rate period and $\frac{V_1}{A}$ is the total volume of filtrate in gal. per sq. ft. of press area at the end of the constant rate period

$$R = \frac{V_1}{A\theta_1} = \frac{9.25}{2.945} = 3.14 \text{ gal. per sq. ft. per hr.}$$

The equation for the test conditions therefore is:

$$\theta = \frac{1}{3.14} \times \frac{V_1}{A} + \frac{0.686}{P^{1-s}} \left[\left(\frac{V}{A} \right)^2 - \left(\frac{V_1}{A} \right)^2 \right]$$

Expressions for the Proposed Press Operations

The general filtration equation expressing the operation of the proposed presses will be:

$$\theta = \frac{1}{3.14 \times 1.5} \times \frac{V_1}{A} + \frac{0.686}{50^{0.9}} \left[\left(\frac{V}{A} \right)^2 - \left(\frac{V_1}{A} \right)^2 \right]$$

Since the rate of filtration for the constant rate period will be $3.14 \times 1.5 = 4.71$ gal. per sq. ft. per hr.

$$\frac{V_1}{A} = \frac{P^{1-s}}{r'v\left(\frac{V_1}{AB}\right)} = \frac{(50)^{0.9}}{1.372 \times 4.71} = 5.225 \text{ gal. per sq. ft.}$$

The filtration equation therefore is:

$$\theta = 1.11 + 0.02027 \left[\left(\frac{V}{A} \right)^2 - 27.3 \right] \leftrightarrow \left(\frac{V}{A} > 5.225 \right) \qquad (1)$$

NOTE: In the equation when $\frac{V}{A} = 5.225$ gal. per sq. ft. (end of the constant rate period) the last term reduces to zero and θ equals 1.11 hrs. (the time of the constant rate period). The length of the constant rate filtration period will therefore be constant (1.11 hrs.) and the total volume of filtrate issuing from the presses during the constant rate period will be 5.225 gal. per sq. ft. of press area.

By differentiating the filtration equation (1) the instantaneous rate of filtration can be found:

$$\theta = 1.11 + 0.02027\left[\left(\frac{V}{A}\right)^2 - 27.3\right]$$

$$d\theta = 0.04054 \times \frac{V}{A}\, d\,\frac{V}{A}$$

$$\frac{d\frac{V}{A}}{d\theta} = \frac{1}{0.04054\left(\frac{V}{A}\right)} = \frac{24.65}{\frac{V}{A}}$$ gal. per sq. ft. per hr. at the end of the const. press. filtration.

The washing rate for a chamber press will be:

$$\left[\frac{d\frac{V}{A}}{d\theta}\right]_{w.ch.} = \frac{24.65}{4\,\frac{V}{A}} = \frac{6.1625}{\frac{V}{A}}$$ gal. per sq. ft. per hr.

The washing rate for a leaf press will be:

$$\left[\frac{d\frac{V}{A}}{d\theta}\right]_{w.lf.} = \frac{24.65}{\frac{V}{A}}$$ gal. per sq. ft. per hr.

CALCULATIONS FOR THE OPERATING CYCLES AND ANNUAL COST OF THE CHAMBER TYPE PRESS

Time expended per cycle:

Filtration ..... $\theta_f = 1.11 + 0.02027\left[\left(\frac{V}{A}\right)^2 - 27.3\right]$

Washing ..... $\theta_w = \frac{\text{vol. wash water}}{\text{rate washing}} =$

$$\frac{\frac{V}{A}}{3 \times \frac{6.1625}{\frac{V}{A}}} = \frac{\left(\frac{V}{A}\right)^2}{18.4875}$$

Cleaning, etc. ..... $\theta_c = 2.5$

The total volume of filtrate per day will be:

$$30{,}000 \times 0.9832 = 29496 \text{ gal.}$$

Let n = the number of cycles per day of 24 hrs.

Then:

$$\frac{24}{n} = 2.5 + 1.11 + 0.02027\left[\left(\frac{V}{A}\right)^2 - 27.3\right] + \left(\frac{V}{A}\right)^2 \times \frac{1}{18.4875}$$

But, $\frac{29496}{n} = V$; therefore

$$\frac{24}{n} = 2.5 + 1.11 + 0.02027\left[\left(\frac{29496}{nA}\right)^2 - 27.3\right] +$$

$$\frac{1}{18.4875}\left[\frac{29496}{nA}\right]^2$$

which reduces to:

$$\frac{24}{n} = 3.057 + \frac{64{,}600{,}000}{n^2A^2}$$

$$\text{or, } 3.057n^2 - 24n + \frac{64{,}600{,}000}{A^2} = 0 \qquad (2)$$

Differentiating equation (2) with respect to n, setting the derivative equal to zero, and solving for n gives a maximum for n of 3.92.

This value of n maximum substituted into equation (2) gives the minimum value of A, which is found to be 1170 sq. ft.

Various values of A, upwards of 1200 sq. ft., and multiples of the given press sizes are then substituted into equation (2) and the corresponding values of n determined.

The results of this calculation are:

A	1200	1400	1500	1800	2000	2100	2500	2700	2800	3600
n	3.072	1.77	1.471	0.945	0.741	0.6675	0.4578	0.389	0.360	0.214

The various values of n thus found are then used in calculating the annual costs for each of the installations.

A sample of this calculation is given below:

Sample Calculation

Total press area = 1800 sq. ft.
Two 900 sq. ft. presses will be used to give this area.
Annual fixed charges—$1800 \times 2.1 \times 0.3 = \$1135$.
Number of cycles per year—$0.945 \times 330 = 311.9$.
Annual cost of filter cloth*—$311.9/60 \times 1800 \times 0.11 = \$1030$.
Annual cleaning and reassembling costs—
$311.9 \times 2.5 \times 0.6 \times 2 = \$935$.

Annual Costs

Fixed charges	\$1135
Filter cloth	1030
Labor for cleaning, etc.	935
Total annual cost	\$3100

The annual cost of each installation is calculated in a similar manner. The results of these calculations are tabulated on the next page.

* No allowance is made here for the amount of filter cloth which is clamped in between the frames and is not actual filtering surface. The actual amount of cloth necessary will be more than 900 sq. ft. per press.

RESULTS OF COST CALCULATIONS

Total filter area sq. ft.	1200	1400	1500	1800	2000	2100	2500	2700	2800	3600
Size of each press	300	700	500	900	500	700	500	900	700	900
Number of presses	4	2	3	2	4	3	5	3	4	4
n	3.07	1.77	1.47	.945	.741	.667	.458	.389	.360	.214
Number of cycles per year	1013	584	485	311.9	244.5	220	151.2	128.3	118.9	70.6
Annual fixed charges	$1080	$966	$1125	$1135	$1500	$1450	$1875	$1710	$1932	$2270
Annual cost of filter cloth	$2230	$1500	$1344	$1030	$896	$847.2	$692.7	$635	$610	$462
Labor for cleaning, etc.	$6075	$1751	$2183	$935	$1468	$990	$1134	$577.5	$713	$424
Total annual costs	$9385	$4217	$4652	$3100	$3864	$3287.2	$3701.7	$2922.5	$3255	$3156

The results show that the most economical installation of chamber presses has a total filtering area of 2700 sq. ft. consisting of three presses of 900 sq. ft. area each.

Since

$$\frac{V}{A} = \frac{29496}{nA}$$

$$\frac{V}{A} = \frac{29496}{0.389 \times 2700} = 28.1 \text{ gal. per sq. ft. per cycle.}$$

Since n equals 0.389

$$\frac{24}{.389} = 61.7 \text{ hrs. per cycle.}$$

The time distribution between the various operations can be calculated by substituting the value of V/A as found above (28.1) in the equations for filtration and washing. The time distribution was found to be as follows:

Constant rate filtration	1.11 hrs.
Constant pressure filtration	15.5 "
Washing	42.6 "
Cleaning and reassembling	2.5 "
Total time per cycle	61.71 hrs.

The thickness of the distance frames will be:

$$t = 1 \times \frac{28.1}{18.19} = 1.544 \text{ inches}$$

Therefore 1½ inch distance frames should be used.

Calculations for the Operating Cycles and Annual Cost of the Leaf Type Press

Time expended per cycle:

Filtration ..... $\theta_f = 1.11 + 0.02027 \left[\left(\frac{V}{A}\right)^2 - 27.3 \right]$

Washing ..... $\theta_w = \frac{\left(\frac{V}{A}\right)^2}{3 \times 24.65} = \frac{\left(\frac{V}{A}\right)^2}{73.95}$

Cleaning and reassembling ..... $\theta_c = 0.75$

Let n equal the number of cycles per day of 24 hrs.

$$\frac{n}{24} = 1.11 + 0.75 - 27.3 \times 0.02027 + \left(\frac{V}{A}\right)^2 \left(0.02027 + \frac{1}{73.95}\right)$$

$$\frac{24}{n} = 1.11 + 0.75 - 0.553 + 0.03379 \left(\frac{V}{A}\right)^2$$

$$\frac{24}{n} = 1.307 + 0.03379 \frac{(29496)^2}{n^2 A^2}$$

$$\frac{24}{n} = 1.307 + \frac{29{,}400{,}000}{n^2 A^2}$$

$$\text{or, } 1.307n^2 - 24n + \frac{29{,}400{,}000}{A^2} = 0 \qquad (3)$$

Differentiating equation (3) with respect to n, setting the derivative equal to zero, and solving the maximum value of n is found to be 9.19.

When this value of n_{max} is substituted into equation (3), the minimum value of A is found. This calculation gives:

$$A_{min} = 516 \text{ sq. ft.}$$

Various values of A are now substituted into equation (3) and the corresponding values of n determined. The values of A used are multiples of 100, upwards of 600 which are possible combinations of the given press sizes.

These calculations give the following results:

A	600	700	900	1000	1200	1400	1500	1800
n	4.5	2.985	1.66	1.317	0.892	0.647	.5665	.3828

The annual costs of these possible press installations are now calculated as follows:

Sample Calculation

Total press area = 1000 sq. ft.

Two presses of 500 sq. ft. area each would be used to obtain this area.

Fixed charges on press ..... $1000 \times 9.6 \times 0.3 = \$2880$

Number of cycles per year ..... $1.317 \times 330 = 434.4$

Annual cost of filter cloth ..... $\frac{434.4}{60} \times 1000 \times 0.11 = \$796$

Labor for cleaning, etc. ..... $434.4 \times 0.75 \times 0.6 \times 2 = \$391$

Annual Costs

Fixed charges	$2880
Filter cloth	796
Labor for cleaning and reassembling	391
Total annual cost	$4067

Similar calculations for the other press sizes gives the results tabulated on the following page.

Total filter area sq. ft.	600	700	900	1000	1200	1400	1800
Size of each press sq. ft.	300	700	900	500	300	700	900
Number of presses	2	1	1	2	4	2	2
n	4.5	2.985	1.66	1.317	0.892	0.647	0.3828
Cycles per year	1485	985.5	547.7	434.4	294.4	213.6	126.3
Annual fixed charges	$1980	$1786	$2026	$2880	$3960	$3570	$4050
Annual cost of filter cloth	$1633	$1266	$904	$796	$647.7	$548	$417.2
Labor for cleaning	$1338	$444	$246.3	$391	$530	$192	$113.8
Total annual costs	$4951	$3496	$3176.3	$4067	$5137.7	$4310	$4581

Total press areas greater than 1800 sq. ft. will give large increases in annual costs because the cost of labor for cleaning and the cost of filter cloth drop only very slowly while the press costs increase rapidly with increase in size. Therefore such installations would not be practical.

The annual costs calculated show that the optimum size is a single leaf press of 900 sq. ft. area.

$$\text{Since } V/A = \frac{29496}{nA} \text{ and } n = 1.66$$

$$\frac{V}{A} = \frac{29496}{nA} = \frac{29496}{1.66 \times 900} = 19.75 \text{ gal. per sq. ft.}$$

$$\frac{24}{n} = \frac{24}{1.66} = 14.46 \text{ hrs. per cycle.}$$

The distribution of the time during the operating cycle is as follows:

Constant rate filtration	1.11	hrs.
Constant pressure filtration	7.34	"
Washing	5.26	"
Cleaning and reassembling	0.75	"
Total time of cycle	14.46	hrs.

CONCLUSIONS

The optimum installation of chamber presses was found to be three presses of 900 sq. ft. area each. The annual cost of the filtration using the chamber presses would be $2922.50.

The optimum installation of leaf presses was found to be a single leaf press of 900 sq. ft. area. The annual cost of the filtration using the leaf press would be $3176.30.

The difference in annual costs of the two installations was found to be $253.80 which is approximately 8.5% of the annual cost of the filtration. Therefore on the basis of the annual cost of the filtration the most economical installation would be that of the three 900 sq. ft. chamber type presses using 1½ inch distance frames.

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